Variational *R*-matrix methods for many-electron systems: Unified nonrelativistic theory

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A nonrelativistic *R*-matrix theory for many-electron systems is formulated in the language of integral operators. A relationship between the operator and matrix formulations is provided. Six variational principles related to the subject are presented. The Rayleigh-Ritz linear trial functions are used in these principles, yielding second-order variational estimates of eigenvalues, elements, and reciprocals of elements of the *R* matrix and its inverse. Following the ideas of Hinze and Hamacher [J. Chem. Phys. **92**, 4372 (1990)], a multiconfiguration Hartree-Fock approach to the *R*-matrix method is proposed.

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I. INTRODUCTION

Despite their considerable usefulness in the analysis of Rydberg spectra, photoionization of complex atoms, and related atomic and molecular phenomena [1–4] variational *R*-matrix methods still seem to be unappreciated in comparison with much more popular *R*-matrix approaches based on ideas of Wigner [5–9]. This state of affairs must be partly attributed to the relative newness of these variational methods and to a lack of their unified mathematical treatment (cf., however, Ref. [10]). It is the goal of the present work to fill this gap.

In this work we shall consider a system composed of N nonrelativistic electrons. These may all be electrons of an atom (or molecule) moving in a Coulomb field produced by an infinitely heavy nucleus (nuclei) or a group of valence electrons moving in an effective field due to an infinitely heavy nucleus (nuclei) and an electronic core. Our considerations will be very general in that we shall not make use of any possible symmetries of the system in order not to obscure the main ideas and the underlying mathematical formalism. Also, we shall not discuss any particular physical process and shall not impose any restrictions on the energy of the system apart from those required by applicability of the nonrelativistic description. Once the ideas and the formalism are understood in general, it will not be difficult to apply them to any specific case when restriction to a particular energy range or exploitation of eventual symmetries of the system may lead to a considerable simplification of the mathematical treatment.

The paper is divided into nine sections. After this introduction, in Sec. II the notation used in the rest of the work is presented. In Sec. III we follow the ideas of Nesbet [11,12] and introduce two mutually reciprocal integral operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ and investigate their properties. It is shown in Sec. IV that matrix representations of these two operators are the commonly used logarithmic derivative matrix $\mathsf{B}(E)$ and the *R*-matrix $\mathsf{R}(E)$. Section V is devoted to a presentation of six variational principles: for eigenvalues, matrix elements, and reciprocals of matrix elements of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$. The principles are given without details of their derivations since the latter are nearly identical to those presented in our earlier works [13,14] concerning the theory for the single-particle case. In Sec. VI we use the Rayleigh-Ritz linear trial functions in the principles discussed earlier and find second-order estimates of matrix elements and eigenvalues of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$. Spectral expansions of kernels of operators approximating $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are also derived. Although basis functions used in the Rayleigh-Ritz expansions may be arbitrary, when dealing with many-electron systems the most convenient choice of these functions is in the form of Slater determinants built of one-electron spin orbitals. Use of such functions is discussed in Sec. VII. Following the ideas of Hinze and Hamacher [15,2], in Sec. VIII we consider the possibility to adapt the multiconfiguration Hartree-Fock technique for a determination of approximate eigenvalues and eigenfunctions of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$. Remarks concluding the paper constitute Sec. IX.

II. DEFINITIONS AND NOTATION

Let $\mathcal{V}\subset\mathbb{R}^3$ be a finite volume enclosed by a surface $\mathcal{S}$. A position vector, relative to some reference origin, of a point in the volume $\mathcal{V}$, will be denoted by $\mathbf{r}$. If the point is located on the surface $\mathcal{S}$, the position vector will be marked with $\boldsymbol{\rho}$. A unit outward vector normal to the surface $\mathcal{S}$ at the point $\boldsymbol{\rho}$ will be denoted by $\mathbf{n}(\boldsymbol{\rho})$.

If $\phi(\mathbf{r})$ and $\phi'(\mathbf{r})$ are any two sufficiently regular two-component spinor functions, their scalar products over $\mathcal{V}$ and $\mathcal{S}$ are defined as

$$\langle\phi|\phi'\rangle\equiv\int_{\mathcal{V}}d^3\mathbf{r}\,\phi^\dagger(\mathbf{r})\phi'(\mathbf{r}) \tag{2.1}$$

and

$$(\phi|\phi')\equiv\oint_{\mathcal{S}}d^2\boldsymbol{\rho}\,\phi^\dagger(\boldsymbol{\rho})\phi'(\boldsymbol{\rho}), \tag{2.2}$$

respectively. Here $d^3\mathbf{r}$ is an infinitesimal volume element of $\mathcal{V}$ around the point $\mathbf{r}$, $d^2\boldsymbol{\rho}$ is an infinitesimal *scalar* surface element of $\mathcal{S}$ around the point $\boldsymbol{\rho}$, and the dagger denotes the

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matrix Hermitian conjugation. A normal outward derivative of the function $\phi(\mathbf{r})$ at the surface point $\boldsymbol{\rho}$ will be denoted by $\partial_n\phi(\boldsymbol{\rho})$.

With the volume $\mathcal{V}\subset\mathbb{R}^3$ one may associate a hypervolume $\mathfrak{V}\subset\mathbb{R}^{3N}$ defined as

$$\mathfrak{V}=\{\mathfrak{r}=[\mathbf{r}_1,\ldots,\mathbf{r}_K,\ldots,\mathbf{r}_N]\in\mathbb{R}^{3N};\forall 1\leqslant K\leqslant N:\mathbf{r}_K\in\mathcal{V}\} \tag{2.3}$$

or, equivalently, as the N-fold Cartesian product of $\mathcal{V}$:

$$\mathfrak{V}=\mathcal{V}^N\equiv\mathcal{V}_1\times\cdots\times\mathcal{V}_N. \tag{2.4}$$

The hypervolume $\mathfrak{V}$ is bounded by a hypersurface $\mathfrak{S}$

$$\mathfrak{S}=\bigcup_{K=1}^{N}\mathcal{V}_1\times\cdots\times\mathcal{V}_{K-1}\times\mathcal{S}_K\times\mathcal{V}_{K+1}\times\cdots\times\mathcal{V}_N. \tag{2.5}$$

If the point $\mathfrak{r}$ lies on the hypersurface $\mathfrak{S}$, we shall denote this using the symbol ϱ instead of $\mathfrak{r}$. A unit outward vector normal to the hypersurface $\mathfrak{S}$ at the point ϱ will be denoted by $\mathbf{n}(\varrho)$.

The hypersurface $\mathfrak{S}$ is composed of N geometrically similar hyperfaces, with the Kth hyperface $\mathfrak{S}_K$ defined as

$$\mathfrak{S}_K=\mathcal{V}_1\times\cdots\times\mathcal{V}_{K-1}\times\mathcal{S}_K\times\mathcal{V}_{K+1}\times\cdots\times\mathcal{V}_N$$

$$(K=1,2,\ldots,N). \tag{2.6}$$

If the point ϱ is on $\mathfrak{S}_K$, we shall indicate this adding the subscript K at ϱ, i.e., writing ϱ_K instead of ϱ. Explicitly,

$$\varrho_K=[\mathbf{r}_1,\ldots,\mathbf{r}_{K-1},\boldsymbol{\rho}_K,\mathbf{r}_{K+1},\ldots,\mathbf{r}_N]. \tag{2.7}$$

It follows from the definition of $\mathcal{S}$ and from Eq. (2.7) that on $\mathfrak{S}_K$ the unit outward normal vector is

$$\mathbf{n}(\varrho_K)=[\mathbf{0}_1,\ldots,\mathbf{0}_{K-1},\mathbf{n}(\boldsymbol{\rho}_K),\mathbf{0}_{K+1},\ldots,\mathbf{0}_N], \tag{2.8}$$

where $\mathbf{n}(\boldsymbol{\rho})$ is a unit outward vector normal to $\mathcal{S}$ at the point $\boldsymbol{\rho}$.

If $\Phi(\mathfrak{r})$ and $\Phi'(\mathfrak{r})$ are sufficiently regular 2^N-component spinor functions defined in $\mathfrak{V}$ and on $\mathfrak{S}$, their scalar products over $\mathfrak{V}$ and over $\mathfrak{S}$ are

$$\langle\Phi|\Phi'\rangle_{\mathfrak{V}}\equiv\int_{\mathfrak{V}}d^{3N}\mathfrak{r}\,\Phi^\dagger(\mathfrak{r})\Phi'(\mathfrak{r}), \tag{2.9}$$

$$(\Phi|\Phi')_{\mathfrak{S}}\equiv\oint_{\mathfrak{S}}d^{3N-1}\varrho\,\Phi^\dagger(\varrho)\Phi'(\varrho), \tag{2.10}$$

respectively, where

$$\int_{\mathfrak{V}}d^{3N}\mathfrak{r}(\cdots)\equiv\int_{\mathcal{V}}d^3\mathbf{r}_1\cdots\int_{\mathcal{V}}d^3\mathbf{r}_N(\cdots) \tag{2.11}$$

and

$$\oint_{\mathfrak{S}}d^{3N-1}\varrho(\cdots)\equiv\sum_{K=1}^{N}\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K(\cdots), \tag{2.12}$$

with

$$\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K(\cdots)\equiv\int_{\mathcal{V}}d^3\mathbf{r}_1\cdots\int_{\mathcal{V}}d^3\mathbf{r}_{K-1}\times\oint_{\mathcal{S}}d^2\boldsymbol{\rho}_K\int_{\mathcal{V}}d^3\mathbf{r}_{K+1}\cdots\int_{\mathcal{V}}d^3\mathbf{r}_N(\cdots). \tag{2.13}$$

Here $d^{3N}\mathfrak{r}$ denotes an infinitesimal element of the hypervolume $\mathfrak{V}$ around the point $\mathfrak{r}$, and $d^{3N-1}\varrho$ is an infinitesimal *scalar* element of the hypersurface $\mathfrak{S}$ around the point ϱ. The scalar product of the functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ over a particular hyperface $\mathfrak{S}_K$ is defined as

$$(\Phi|\Phi')_{\mathfrak{S}_K}\equiv\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K\,\Phi^\dagger(\varrho_K)\Phi'(\varrho_K). \tag{2.14}$$

From Eqs. (2.10), (2.12), and (2.14), one has

$$(\Phi|\Phi')_{\mathfrak{S}}=\sum_{K=1}^{N}(\Phi|\Phi')_{\mathfrak{S}_K}. \tag{2.15}$$

A space of all completely antisymmetric 2^N-component spinor functions $\Phi(\mathfrak{r})$ defined in the hypervolume $\mathfrak{V}$ and such that $\langle\Phi|\Phi\rangle_{\mathfrak{V}}<\infty$ will be denoted by $\mathcal{A}_{\mathfrak{V}}$. The projector on the space of such functions (the hypervolume antisymmetrizer) will be marked with $\hat{\mathcal{A}}_{\mathfrak{V}}$. A class of functions from $\mathcal{A}_{\mathfrak{V}}$ that are twice differentiable in $\mathfrak{V}$ will be designed with $\mathcal{A}''_{\mathfrak{V}}$. A space of all completely antisymmetric functions $\Phi(\varrho)$ defined on the hypersurface $\mathfrak{S}$ and such that $(\Phi|\Phi)_{\mathfrak{S}}<\infty$ will be denoted by $\mathcal{A}_{\mathfrak{S}}$; the projector on the space of such functions (the hypersurface antisymmetrizer) will be marked with $\hat{\mathcal{A}}_{\mathfrak{S}}$.

If $\Phi(\varrho)$ and $\Phi'(\varrho)$ are any two functions from $\mathcal{A}_{\mathfrak{S}}$, from their antisymmetry and from the geometric similarity of any two hyperfaces $\mathfrak{S}_K$ and $\mathfrak{S}_{K'}$, one infers that

$$\forall 1\leqslant K,K'\leqslant N:(\Phi|\Phi')_{\mathfrak{S}_K}=(\Phi|\Phi')_{\mathfrak{S}_{K'}}$$

$$(\Phi(\varrho),\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}) \tag{2.16}$$

and consequently [cf. Eq. (2.15)]

$$\forall 1\leqslant K\leqslant N:(\Phi|\Phi')_{\mathfrak{S}_K}=\frac{1}{N}(\Phi|\Phi')_{\mathfrak{S}}$$

$$(\Phi(\varrho),\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}). \tag{2.17}$$

III. OPERATORS $\hat{\mathcal{B}}(E)$ AND $\hat{\mathcal{R}}(E)$

Consider a system of N nonrelativistic electrons described by the Hamiltonian

$$\hat{\mathcal{H}}(\mathfrak{r})=\sum_{K=1}^{N}\hat{H}(\mathbf{r}_K)+\frac{1}{2}\sum_{\substack{K,K'=1\\(K\neq K')}}^{N}\hat{U}(\mathbf{r}_K,\mathbf{r}_{K'})$$
$$=\sum_{K=1}^{N}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_K^2+\hat{V}(\mathbf{r}_K)\right)+\frac{1}{2}\sum_{\substack{K,K'=1\\(K\neq K')}}^{N}\hat{U}(\mathbf{r}_K,\mathbf{r}_{K'}). \tag{3.1}$$

In this definition, $\mathbf{r}_K$ is a position vector of the Kth electron in the three-dimensional physical space (relative to an origin common to all the electrons) while $\boldsymbol{\nabla}_K$ is a gradient operator with respect to coordinates of the Kth electron. The symbol $\mathfrak{r}=[\mathbf{r}_1,\ldots,\mathbf{r}_N]$ denotes a position hypervector of a point describing a configuration of the system in an abstract $3N$-dimensional configuration space, and we shall use the symbol $\boldsymbol{\nabla}=[\boldsymbol{\nabla}_1,\ldots,\boldsymbol{\nabla}_N]$ to denote the hypergradient operator with respect to components of $\mathfrak{r}$. The multiplicative potential operators $\hat{V}(\mathbf{r}_K)$ and $\hat{U}(\mathbf{r}_K,\mathbf{r}_{K'})$ are real scalar (i.e., spin-independent) functions of electronic spatial coordinates with the function $\hat{U}(\mathbf{r}_K,\mathbf{r}_{K'})$ being symmetric in its arguments.

The time-independent Schrödinger equation for the system under consideration is

$$[\hat{\mathcal{H}}(\mathfrak{r})-E]\Psi(E,\mathfrak{r})=0, \tag{3.2}$$

where E is the total electronic energy of the system. Since we are dealing with electrons, we shall conform to Pauli's exclusion principle and consider only those solutions to Eq. (3.2) which are completely antisymmetric 2^N-component spinors. In what follows, we shall assume that the electronic energy E is fixed at some prescribed real value, and consider those configurations of the system where all N electrons are in some fictitious finite volume $\mathcal{V}$ enclosed by a surface $\mathcal{S}$. Then the configuration point $\mathfrak{r}$ lies in the corresponding (fictitious) hypervolume $\mathfrak{V}$ defined by Eq. (2.4) and bounded by the hypersurface $\mathfrak{S}$ defined by Eq. (2.5). We emphasize that we do not confine the electrons to the volume $\mathcal{V}$ in any way since we do not impose any artificial boundary condition on the wave function $\Psi(E,\mathfrak{r})$ at $\mathfrak{S}$.

We shall denote by $\mathcal{A}_{\mathfrak{V}}(E)$ a subspace of $\mathcal{A}_{\mathfrak{V}}$ built of all completely antisymmetric regular solutions to the Schrödinger equation (3.2) in the hypervolume $\mathfrak{V}$ at the real energy E; the projector on this subspace will be denoted by $\hat{\mathcal{A}}_{\mathfrak{V}}(E)$. Let $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$ and $\Psi'(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$. In virtue of the reality of E, we have

$$\langle\hat{\mathcal{H}}\Psi'|\Psi\rangle_{\mathfrak{V}}-\langle\Psi'|\hat{\mathcal{H}}\Psi\rangle_{\mathfrak{V}}=0, \tag{3.3}$$

which means that the Hamiltonian $\hat{\mathcal{H}}(\mathfrak{r})$ is Hermitian on $\mathcal{A}_{\mathfrak{V}}(E)$. On the other hand, application of the $3N$-dimensional Green integration theorem to the expression on the left-hand side of Eq. (3.3) yields

$$\langle\hat{\mathcal{H}}\Psi'|\Psi\rangle_{\mathfrak{V}}-\langle\Psi'|\hat{\mathcal{H}}\Psi\rangle_{\mathfrak{V}}=\frac{\hbar^2}{2m}(\Psi'|\nabla_n\Psi)_{\mathfrak{S}}-\frac{\hbar^2}{2m}(\nabla_n\Psi'|\Psi)_{\mathfrak{S}}, \tag{3.4}$$

where

$$\nabla_n\Psi(E,\varrho)=\mathfrak{n}(\varrho)\cdot\boldsymbol{\nabla}\Psi(E,\varrho) \tag{3.5}$$

denotes the normal derivative of the function $\Psi(E,\mathfrak{r})$ at the point ϱ on the hypersurface $\mathfrak{S}$. Equations (3.3) and (3.4) imply

$$(\Psi'|\nabla_n\Psi)_{\mathfrak{S}}=(\nabla_n\Psi'|\Psi)_{\mathfrak{S}}. \tag{3.6}$$

We define a linear integral operator $\hat{\mathcal{B}}(E)$ such that

$$\nabla_n\Psi(E,\varrho)=\hat{\mathcal{B}}(E)\Psi(E,\varrho) \tag{3.7}$$

for any $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$. The operator $\hat{\mathcal{B}}(E)$ is represented by its integral kernel $\mathcal{B}(E,\varrho,\varrho')$ which is simultaneously a function of the hypersurface coordinates ϱ and ϱ' and a square $2^N\times 2^N$ matrix in the joint N-electron spin space. In terms of the kernel $\mathcal{B}(E,\varrho,\varrho')$, Eq. (3.7) reads

$$\nabla_n\Psi(E,\varrho)=\oint_{\mathfrak{S}}d^{3N-1}\varrho'\mathcal{B}(E,\varrho,\varrho')\Psi(E,\varrho'). \tag{3.8}$$

Substitution of Eq. (3.7) into relation (3.6) gives

$$(\hat{\mathcal{B}}\Psi'|\Psi)_{\mathfrak{S}}=(\Psi'|\hat{\mathcal{B}}\Psi)_{\mathfrak{S}}, \tag{3.9}$$

which means that the operator $\hat{\mathcal{B}}(E)$ is Hermitian with respect to the scalar product $(|)_{\mathfrak{S}}$. Consequently, its kernel possesses the symmetry property

$$\mathcal{B}(E,\varrho,\varrho')=\mathcal{B}^{\dagger}(E,\varrho',\varrho). \tag{3.10}$$

The left-hand side of Eq. (3.7) remains invariant after operating on it from the left with the antisymmetrizer $\hat{\mathcal{A}}_{\mathfrak{S}}$, and this implies that

$$\hat{\mathcal{B}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}\hat{\mathcal{B}}(E). \tag{3.11}$$

Since $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{A}}_{\mathfrak{S}}$ are Hermitian under the scalar product $(|)_{\mathfrak{S}}$, one infers that

$$\hat{\mathcal{B}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}\hat{\mathcal{B}}(E)\hat{\mathcal{A}}_{\mathfrak{S}}, \tag{3.12}$$

which means that the operator $\hat{\mathcal{B}}(E)$ is symmetric in all the N electrons.

Consider now a set $\{\Psi_k(E,\mathfrak{r})\}\subset\mathcal{A}_{\mathfrak{V}}(E)$ of functions which on the hypersurface $\mathfrak{S}$ satisfy

$$\nabla_n\Psi_k(E,\varrho)=b_k(E)\Psi_k(E,\varrho), \tag{3.13}$$

where $b_k(E)$ is a number associated with the function $\Psi_k(E,\varrho)$. On combining Eq. (3.13) with definition (3.7), we obtain

$$\hat{\mathcal{B}}(E)\Psi_k(E,\varrho)=b_k(E)\Psi_k(E,\varrho), \tag{3.14}$$

which means that the numbers $\{b_k(E)\}$ are eigenvalues of the operator $\hat{\mathcal{B}}(E)$, and the hypersurface functions $\{\Psi_k(E,\varrho)\}$ are corresponding eigenfunctions. Since the operator $\hat{\mathcal{B}}(E)$ is Hermitian, all eigenvalues $\{b_k(E)\}$ are real, and eigenfunctions associated with different eigenvalues are mutually orthogonal in the sense of

$$(\Psi_k|\Psi_l)_{\mathfrak{S}}=0 \quad (b_k(E)\neq b_l(E)). \tag{3.15}$$

Eigenfunctions associated with degenerate eigenvalues (if there are any) may also be orthogonalized, and it is convenient to normalize all eigenfunctions so that

$$(\Psi_k|\Psi_l)_{\mathfrak{S}}=\delta_{kl} \tag{3.16}$$

for any pair of the indices k,l. For the sake of later use, we notice here that, with the aid of Eq. (3.13), the orthogonality relation (3.16) may be equivalently rewritten in the form

$$(\nabla_n\Psi_k|\nabla_n\Psi_l)_{\mathfrak{S}}=b_k^2(E)\,\delta_{kl}\,. \tag{3.17}$$

In terms of its eigenfunctions and eigenvalues, the spectral expansion of the kernel $\mathcal{B}(E,\varrho,\varrho')$ is

$$\mathcal{B}(E,\varrho,\varrho')=\sum_k\ \Psi_k(E,\varrho)b_k(E)\Psi_k^\dagger(E,\varrho'). \tag{3.18}$$

Equivalently, on using Eq. (3.13), expansion (3.18) may be rewritten in the form

$$\mathcal{B}(E,\varrho,\varrho')=\sum_k\ \nabla_n\Psi_k(E,\varrho)b_k^{-1}(E)\nabla_n\Psi_k^\dagger(E,\varrho'). \tag{3.19}$$

The functions $\{\Psi_k(E,\mathfrak{r})\}$ form a complete set in the subspace $\mathcal{A}_{\mathfrak{V}}(E)$, and any function $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$ may be expanded in this set according to

$$\Psi(E,\mathfrak{r})=\sum_k\ c_k(E)\Psi_k(E,\mathfrak{r}), \tag{3.20}$$

with the expansion coefficients given by

$$c_k(E)=(\Psi_k|\Psi)_{\mathfrak{S}}\,. \tag{3.21}$$

On the hypersurface $\mathfrak{S}$, Eq. (3.20) reads

$$\Psi(E,\varrho)=\sum_k\ c_k(E)\Psi_k(E,\varrho). \tag{3.22}$$

Equations (3.21) and (3.22) imply that the relation

$$\mathcal{A}_{\mathfrak{S}}(E,\varrho,\varrho')=\sum_k\ \Psi_k(E,\varrho)\Psi_k^\dagger(E,\varrho') \tag{3.23}$$

defines the kernel of a linear integral operator $\hat{\mathcal{A}}_{\mathfrak{S}}(E)$ such that for any $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$:

$$\hat{\mathcal{A}}_{\mathfrak{S}}(E)\Psi(E,\varrho)=\Psi(E,\varrho). \tag{3.24}$$

Since the operator $\hat{\mathcal{A}}_{\mathfrak{S}}(E)$ is evidently Hermitian under the scalar product $(|)_{\mathfrak{S}}$, and since, on using Eqs. (3.23) and (3.16), it is readily verifiable that

$$\hat{\mathcal{A}}_{\mathfrak{S}}^2(E)=\hat{\mathcal{A}}_{\mathfrak{S}}(E), \tag{3.25}$$

we conclude that the operator $\hat{\mathcal{A}}_{\mathfrak{S}}(E)$ is the projector on a subspace $\mathcal{A}_{\mathfrak{S}}(E)\subset\mathcal{A}_{\mathfrak{S}}$ defined as

$$\mathcal{A}_{\mathfrak{S}}(E)=\{\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}};\exists\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E):\ \Phi(\varrho)=\Psi(E,\varrho)\}. \tag{3.26}$$

For the sake of later comparison (cf. Sec. VI D) we notice at this moment that, with the aid of Eq. (3.13), the defining relation (3.23) may be rewritten equivalently as

$$\mathcal{A}_{\mathfrak{S}}(E,\varrho,\varrho')=\sum_k\ \nabla_n\Psi_k(E,\varrho)b_k^{-2}(E)\nabla_n\Psi_k^\dagger(E,\varrho'). \tag{3.27}$$

We define the linear integral operator $\hat{\mathcal{R}}(E)$, symmetric in all the N electrons and possessing the property

$$\hat{\mathcal{R}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}\hat{\mathcal{R}}(E)\hat{\mathcal{A}}_{\mathfrak{S}}, \tag{3.28}$$

analogous to that expressed by Eq. (3.12), as the operator reciprocal to $\hat{\mathcal{B}}(E)$ in the sense of

$$\hat{\mathcal{R}}(E)\hat{\mathcal{B}}(E)=\hat{\mathcal{B}}(E)\hat{\mathcal{R}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}(E). \tag{3.29}$$

The operator $\hat{\mathcal{R}}(E)$ is Hermitian with respect to the scalar product $(|)_{\mathfrak{S}}$, and is represented by the integral kernel $\mathcal{R}(E,\varrho,\varrho')$, in terms of which the reciprocity relation (3.29) reads

$$\begin{aligned}\oint_{\mathfrak{S}}d^{3N-1}\varrho''\mathcal{R}(E,\varrho,\varrho'')\mathcal{B}(E,\varrho'',\varrho')&=\oint_{\mathfrak{S}}d^{3N-1}\varrho''\mathcal{B}(E,\varrho,\varrho'')\mathcal{R}(E,\varrho'',\varrho')\\&=\mathcal{A}_{\mathfrak{S}}(E,\varrho,\varrho').\end{aligned} \tag{3.30}$$

On using the operator $\hat{\mathcal{R}}(E)$, Eqs. (3.7) and (3.8) may be converted into

$$\Psi(E,\varrho)=\hat{\mathcal{R}}(E)\nabla_n\Psi(E,\varrho) \tag{3.31}$$

and

$$\Psi(E,\varrho)=\oint_{\mathfrak{S}}d^{3N-1}\varrho'\mathcal{R}(E,\varrho,\varrho')\nabla_n'\Psi(E,\varrho'), \tag{3.32}$$

respectively.

Operating on both sides of Eq. (3.14) with $\hat{\mathcal{R}}(E)$, using relations (3.29) and (3.24), and performing an elementary transformation of the resulting equation, one finds

$$\hat{\mathcal{R}}(E)\Psi_k(E,\varrho)=b_k^{-1}(E)\Psi_k(E,\varrho), \tag{3.33}$$

which means that the functions $\{\Psi_k(E,\varrho)\}$ are also eigenfunctions of the operator $\hat{\mathcal{R}}(E)$ associated with eigenvalues $\{b_k^{-1}(E)\}$. In terms of its eigenfunctions and eigenvalues, the spectral expansion of the kernel $\mathcal{R}(E,\varrho,\varrho')$ is

$$\mathcal{R}(E,\varrho,\varrho')=\sum_k \Psi_k(E,\varrho)b_k^{-1}(E)\Psi_k^\dagger(E,\varrho'). \tag{3.34}$$

After Eq. (3.13) is used, expansion (3.34) may be transformed to the form

$$\mathcal{R}(E,\varrho,\varrho')=\sum_k \nabla_n\Psi_k(E,\varrho)b_k^{-3}(E)\nabla_n\Psi_k^\dagger(E,\varrho'). \tag{3.35}$$

We conclude this section with an observation that the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ possess not only the properties (3.12) and (3.28), respectively, but also the properties

$$\hat{\mathcal{B}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}(E)\hat{\mathcal{B}}(E)\hat{\mathcal{A}}_{\mathfrak{S}}(E), \tag{3.36}$$

$$\hat{\mathcal{R}}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}(E)\hat{\mathcal{R}}(E)\hat{\mathcal{A}}_{\mathfrak{S}}(E), \tag{3.37}$$

which are the consequences of Eqs. (3.18), (3.34), and (3.24).

IV. MATRIX REPRESENTATIONS OF THE OPERATORS $\hat{\mathcal{B}}(E)$ AND $\hat{\mathcal{R}}(E)$

Presume that a basis set $\{\Phi_i(\varrho)\}$, orthonormal under the scalar product $(|)_{\mathfrak{S}}$, is given in $\mathcal{A}_{\mathfrak{S}}(E)$. In this basis the kernels $\mathcal{B}(E,\varrho,\varrho')$ and $\mathcal{R}(E,\varrho,\varrho')$ possess the bilinear expansions

$$\mathcal{B}(E,\varrho,\varrho')=\sum_{i,j}\Phi_i(\varrho)(\Phi_i|\hat{\mathcal{B}}\Phi_j)_{\mathfrak{S}}\Phi_j^\dagger(\varrho'), \tag{4.1}$$

$$\mathcal{R}(E,\varrho,\varrho')=\sum_{i,j}\Phi_i(\varrho)(\Phi_i|\hat{\mathcal{R}}\Phi_j)_{\mathfrak{S}}\Phi_j^\dagger(\varrho'), \tag{4.2}$$

respectively. The expansion coefficients

$$(\Phi_i|\hat{\mathcal{B}}\Phi_j)_{\mathfrak{S}} \equiv \oint_{\mathfrak{S}} d^{3N-1}\varrho \oint_{\mathfrak{S}} d^{3N-1}\varrho'\Phi_i^\dagger(\varrho)\mathcal{B}(E,\varrho,\varrho')\Phi_j(\varrho'), \tag{4.3}$$

$$(\Phi_i|\hat{\mathcal{R}}\Phi_j)_{\mathfrak{S}} \equiv \oint_{\mathfrak{S}} d^{3N-1}\varrho \oint_{\mathfrak{S}} d^{3N-1}\varrho'\Phi_i^\dagger(\varrho)\mathcal{R}(E,\varrho,\varrho')\Phi_j(\varrho') \tag{4.4}$$

form square matrices $\mathsf{B}(E)$ and $\mathsf{R}(E)$, respectively, related through the matrix representation of Eq. (3.29),

$$\mathsf{R}(E)\mathsf{B}(E)=\mathsf{B}(E)\mathsf{R}(E)=\mathsf{I}, \tag{4.5}$$

the right-hand side of which follows from the fact that in any orthonormal basis in $\mathcal{A}_{\mathfrak{S}}(E)$ the projector $\hat{\mathcal{A}}_{\mathfrak{S}}(E)$ is represented by the unit matrix I.

In the literature of the subject, the matrix $\mathsf{R}(E)$ is known as ''the *R* matrix for the Schrödinger equation (3.2) at energy *E*, in the basis $\{\Phi_i(\varrho)\}$ spanning $\mathcal{A}_{\mathfrak{S}}(E)$.'' The matrix $\mathsf{B}(E)$, sometimes denoted by the symbol $\mathsf{Y}(E)$ instead of $\mathsf{B}(E)$, is, as implied by Eq. (4.5), the inverse of $\mathsf{R}(E)$ and is known as ''the logarithmic derivative matrix.''

Matrix representations of the relations (3.7) and (3.31) are

$$\mathsf{D}(E)=\mathsf{B}(E)\mathsf{P}(E) \tag{4.6}$$

and

$$\mathsf{P}(E)=\mathsf{R}(E)\mathsf{D}(E), \tag{4.7}$$

respectively, where $\mathsf{P}(E)$ and $\mathsf{D}(E)$ are column vectors with elements

$$P_i(E)=(\Phi_i|\Psi)_{\mathfrak{S}} \tag{4.8}$$

and

$$D_i(E)=(\Phi_i|\nabla_n\Psi)_{\mathfrak{S}}, \tag{4.9}$$

respectively. The matrix counterparts of the eigenvalue equations (3.14) and (3.33) are

$$\mathsf{B}(E)\mathsf{P}_k(E)=b_k(E)\mathsf{P}_k(E), \tag{4.10}$$

$$\mathsf{R}(E)\mathsf{P}_k(E)=b_k^{-1}(E)\mathsf{P}_k(E), \tag{4.11}$$

respectively, where the eigenvectors $\{\mathsf{P}_k(E)\}$ have components

$$P_{ik}(E)=(\Phi_i|\Psi_k)_{\mathfrak{S}}, \tag{4.12}$$

while the counterparts of the spectral expansions (3.18) and (3.34) are

$$\mathsf{B}(E)=\sum_k \mathsf{P}_k(E)b_k(E)\mathsf{P}_k^\dagger(E), \tag{4.13}$$

$$\mathsf{R}(E)=\sum_k \mathsf{P}_k(E)b_k^{-1}(E)\mathsf{P}_k^\dagger(E), \tag{4.14}$$

respectively.

V. VARIATIONAL PRINCIPLES FOR EIGENVALUES, MATRIX ELEMENTS, AND INVERSES OF MATRIX ELEMENTS OF THE OPERATORS $\hat{\mathcal{B}}(E)$ AND $\hat{\mathcal{R}}(E)$

In this section we present six variational principles related to the *R*-matrix theory of many-electron systems. Listed in the order of their presentation, these are variational principles for eigenvalues of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, variational principles for matrix elements of these operators, and variational principles for reciprocals of matrix elements

of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$. The principles are presented here without derivations: all of them may be obtained in a systematic manner generalizing in the obvious way the author's construction of parallel principles in the single-particle case [13,14].

A. Variational principle for eigenvalues of the operator $\hat{\mathcal{B}}(E)$

The variational principle for eigenvalues of the operator $\hat{\mathcal{B}}(E)$ is

$$b(E)=\underset{\overline{\Psi}}{\mathrm{stat}}\left\{\frac{(\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}+\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}\right\}. \tag{5.1}$$

The trial function $\overline{\Psi}(\mathfrak{r})$ is to be varied in $\mathcal{A}''_{\mathfrak{V}}$; no other restrictions need to be imposed on $\overline{\Psi}(\mathfrak{r})$. Stationary points of the functional in Eq. (5.1) are eigenvalues of $\hat{\mathcal{B}}(E)$, while trial functions which yield these values are those solutions to the Schrödinger equation (3.2) which on the hypersurface $\mathfrak{S}$ are corresponding eigenfunctions of $\hat{\mathcal{B}}(E)$. If the trial function $\overline{\Psi}(\mathfrak{r})$ is varied freely, the principle provides *all* eigenvalues and eigenfunctions of $\hat{\mathcal{B}}(E)$; for that reason we have not added any subscript at $b(E)$ on the left of Eq. (5.1). The principle (5.1) has the advantage in yielding *real* estimates of eigenvalues $\{b_k(E)\}$ for *any* particular trial function used.

In the literature of the subject the principle (5.1) is known as Kohn's principle. Its one-dimensional analog was presented by Kohn in his seminal paper [16] on variational methods in quantum scattering theory. At present the principle (5.1) is the starting point for variational eigenchannel *R*-matrix studies of atomic photoionization processes [17,2] and of Rydberg spectra of complex atoms [3].

B. Variational principle for eigenvalues of the operator $\hat{\mathcal{R}}(E)$

The variational principle

$$b^{-1}(E)=\underset{\overline{\Psi}}{\mathrm{stat}}\left\{\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}}\right\}. \tag{5.2}$$

yields all eigenvalues and eigenfunctions of the operator $\hat{\mathcal{R}}(E)$ if the trial function $\overline{\Psi}(\mathfrak{r})$ is varied freely in $\mathcal{A}''_{\mathfrak{V}}$. The value of the functional on the right side of Eq. (5.2) is real for any admissible trial function. To the best of our knowledge, the principle (5.2) has never been discussed before.

C. Variational principle for matrix elements of the operator $\hat{\mathcal{B}}(E)$

Let $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ [these functions need not be orthonormal with respect to the scalar product $(|)_{\mathfrak{S}}$]. The variational principle for the matrix element $(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}$ has the form

$$(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}=\underset{\overline{\Psi},\overline{\Psi}'}{\mathrm{stat}}\left\{(\Phi|\nabla_n\overline{\Psi}')_{\mathfrak{S}}+(\nabla_n\overline{\Psi}|\Phi')_{\mathfrak{S}}-(\nabla_n\overline{\Psi}|\overline{\Psi}')_{\mathfrak{S}}+\frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}}\right\}. \tag{5.3}$$

The trial functions $\overline{\Psi}(\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})$ may be varied freely in $\mathcal{A}''_{\mathfrak{V}}$. The functional on the right side of Eq. (5.3) reaches its stationary value for $\overline{\Psi}(\mathfrak{r})=\Psi(E,\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})=\Psi'(E,\mathfrak{r})$, where $\Psi(E,\mathfrak{r})$ and $\Psi'(E,\mathfrak{r})$ are these particular completely antisymmetric solutions to the Schrödinger equation (3.2) which on the hypersurface $\mathfrak{S}$ obey the boundary conditions

$$\Psi(E,\varrho)=\Phi(\varrho),\quad \Psi'(E,\varrho)=\Phi'(\varrho), \tag{5.4}$$

respectively. It is to be stressed that the trial functions $\overline{\Psi}(\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})$ need *not* satisfy boundary relations analogous to those in Eq. (5.4). If, however, they are subjected to such constraints, i.e., if

$$\overline{\Psi}(\varrho)=\Phi(\varrho),\quad \overline{\Psi}'(\varrho)=\Phi'(\varrho), \tag{5.5}$$

the second and the third terms in the functional (5.3) cancel and we arrive at the restricted variational principle

$$(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}=\underset{\overline{\Psi},\overline{\Psi}'}{\mathrm{stat}}\left\{(\overline{\Psi}|\nabla_n\overline{\Psi}')_{\mathfrak{S}}+\frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}}\right\}. \tag{5.6}$$

The latter principle was discussed by Altick [18], who applied it to a problem modeling elastic scattering of electrons from hydrogen atoms. We are not aware of any presentation of the more general principle (5.3).

D. Variational principle for matrix elements of the operator $\hat{\mathcal{R}}(E)$

Let $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$. The variational principle for the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}$ is

$$(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}=\underset{\overline{\Psi},\overline{\Psi}'}{\mathrm{stat}}\left\{(\Phi|\overline{\Psi}')_{\mathfrak{S}}+(\overline{\Psi}|\Phi')_{\mathfrak{S}}-(\overline{\Psi}|\nabla_n\overline{\Psi}')_{\mathfrak{S}}-\frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}\right\}. \tag{5.7}$$

The trial functions $\overline{\Psi}(\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})$ may be any functions from $\mathcal{A}''_{\mathfrak{V}}$. The stationary value of the functional in Eq. (5.7) is obtained for $\overline{\Psi}(\mathfrak{r})=\Psi(E,\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})=\Psi'(E,\mathfrak{r})$, with $\Psi(E,\mathfrak{r})$ and $\Psi'(E,\mathfrak{r})$ denoting those particular completely antisymmetric solutions to the Schrödinger equation (3.2) which on the hypersurface $\mathfrak{S}$ satisfy the boundary conditions

$$\nabla_n\Psi(E,\varrho)=\Phi(\varrho),\quad \nabla_n\Psi'(E,\varrho)=\Phi'(\varrho), \tag{5.8}$$

respectively. The trial functions $\overline{\Psi}(\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})$ need *not* satisfy conditions analogous to these in Eq. (5.8). If, however, the constraints

$$\nabla_n\overline{\Psi}(\varrho)=\Phi(\varrho), \quad \nabla_n\overline{\Psi}'(\varrho)=\Phi'(\varrho) \tag{5.9}$$

are imposed, principle (5.7) reduces to

$$(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}=\underset{\overline{\Psi},\overline{\Psi}'}{\text{stat}}\left\{(\nabla_n\overline{\Psi}|\overline{\Psi}')_{\mathfrak{S}}-\frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}}\right\}. \tag{5.10}$$

Principle (5.7) was considered by Shimamura [19] in the context of *R*-matrix theory of electron-atom collisions. The restricted principle (5.10) was proposed earlier, within the framework of the nuclear collision theory, by Jackson [20].

E. Variational principle for reciprocals of matrix elements of the operator $\hat{\mathcal{B}}(E)$

The variational principle for reciprocals of matrix elements of the operator $\hat{\mathcal{B}}(E)$ between the functions $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ is

$$(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}^{-1}=\underset{\overline{\Psi},\overline{\Psi}'}{\text{stat}}\left\{\frac{(\nabla_n\overline{\Psi}|\overline{\Psi}')_{\mathfrak{S}}}{(\Phi|\nabla_n\overline{\Psi}')_{\mathfrak{S}}(\nabla_n\overline{\Psi}|\Phi')_{\mathfrak{S}}}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}}}{(\Phi|\nabla_n\overline{\Psi}')_{\mathfrak{S}}(\nabla_n\overline{\Psi}|\Phi')_{\mathfrak{S}}}\right\}, \tag{5.11}$$

where $\overline{\Psi}(\mathfrak{r})\in\mathcal{A}''_{\mathfrak{V}}$ and $\overline{\Psi}'(\mathfrak{r})\in\mathcal{A}''_{\mathfrak{V}}$. The stationary value is obtained for $\overline{\Psi}(\mathfrak{r})=\eta\Psi(E,\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})=\eta'\Psi'(E,\mathfrak{r})$, where $\Psi(E,\mathfrak{r})$ and $\Psi'(E,\mathfrak{r})$ are completely antisymmetric solutions to the Schrödinger equation (3.2) at energy E obeying the boundary conditions (5.4), while η and η' are arbitrary nonzero complex numbers. The principle was discussed by Nesbet [12].

F. Variational principle for reciprocals of matrix elements of the operator $\hat{\mathcal{R}}(E)$

Let $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$. The variational principle for the inverses of matrix elements of the operator $\hat{\mathcal{R}}(E)$ is

$$(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}^{-1}=\underset{\overline{\Psi},\overline{\Psi}'}{\text{stat}}\left\{\frac{(\overline{\Psi}|\nabla_n\overline{\Psi}')_{\mathfrak{S}}}{(\Phi|\overline{\Psi}')_{\mathfrak{S}}(\overline{\Psi}|\Phi')_{\mathfrak{S}}}+\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}}}{(\Phi|\overline{\Psi}')_{\mathfrak{S}}(\overline{\Psi}|\Phi')_{\mathfrak{S}}}\right\}. \tag{5.12}$$

The variational functions $\overline{\Psi}(\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})$ are from $\mathcal{A}''_{\mathfrak{V}}$. The stationary value is reached for $\overline{\Psi}(\mathfrak{r})=\eta\Psi(E,\mathfrak{r})$ and $\overline{\Psi}'(\mathfrak{r})=\eta'\Psi'(E,\mathfrak{r})$, where $\Psi(E,\mathfrak{r})$ and $\Psi'(E,\mathfrak{r})$ are completely antisymmetric solutions to the Schrödinger equation (3.2) at energy E obeying the boundary conditions (5.8) while η and η' are arbitrary nonzero complex numbers. The principle was discussed by Nesbet [11] in the context of solid-state physics.

VI. DERIVATION OF VARIATIONAL ESTIMATES FOR MATRIX ELEMENTS AND EIGENVALUES OF THE OPERATORS $\hat{\mathcal{R}}(E)$ AND $\hat{\mathcal{B}}(E)$ WITH THE USE OF LINEAR TRIAL FUNCTIONS

In the preceding sections our approach to the *R*-matrix theory has been formal. In the rest of this work we shall be concerned with practical aspects of the theory, and show how the variational principles of Sec. V, together with the knowledge gained in Sec. III, may be used for approximating eigenvalues, matrix elements, and integral kernels of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$. We shall exploit the fact that the variational functionals presented in Sec. V are ideally suited for applications of linear trial functions of the Rayleigh-Ritz type.

A. Estimates of matrix elements of $\hat{\mathcal{R}}(E)$

We shall approximate the solutions to the Schrödinger equation (3.2), satisfying the Neumann boundary conditions (5.8), by linear combinations of n sufficiently regular functions $\{\Theta_i(\mathfrak{r})\}$ chosen from $\mathcal{A}''_{\mathfrak{V}}$,

$$\overline{\Psi}(\mathfrak{r})=\sum_{i=1}^{n}\overline{c_i}\Theta_i(\mathfrak{r}), \quad \overline{\Psi}'(\mathfrak{r})=\sum_{i=1}^{n}\overline{c_i'}\Theta_i(\mathfrak{r}), \tag{6.1}$$

where $\{\overline{c_i}\}$ and $\{\overline{c_i'}\}$ are yet unknown coefficients which remain to be determined. Substitution of the trial functions (6.1) into the functional

$$F[\Phi,\Phi';\overline{\Psi},\overline{\Psi}']=(\Phi|\overline{\Psi}')_{\mathfrak{S}}+(\overline{\Psi}|\Phi')_{\mathfrak{S}}-(\overline{\Psi}|\nabla_n\overline{\Psi}')_{\mathfrak{S}}-\frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}} \tag{6.2}$$

[cf. the right side of Eq. (5.7)] yields

$$F[\mathsf{f}^\dagger,\mathsf{f}';\overline{\mathsf{c}}^\dagger,\overline{\mathsf{c}}']=\mathsf{f}^\dagger\overline{\mathsf{c}}'+\overline{\mathsf{c}}^\dagger\mathsf{f}'-\overline{\mathsf{c}}^\dagger\mathsf{S}\overline{\mathsf{c}}', \tag{6.3}$$

where $\mathsf{f}^\dagger$ and $\overline{\mathsf{c}}^\dagger$ are n-component row matrices with elements $\{f_i^*=(\Phi|\Theta_i)_{\mathfrak{S}}\}$ and $\{\overline{c_i}^*\}$, respectively, f' and $\overline{\mathsf{c}}'$ are n-component column matrices with elements $\{f_i'=(\Theta_i|\Phi')_{\mathfrak{S}}\}$ and $\{\overline{c_i'}\}$, respectively, and $\mathsf{S}(E)$ is a Hermitian $n\times n$ matrix with elements

$$S_{ij}(E)=(\Theta_i|\nabla_n\Theta_j)_{\mathfrak{S}}+\frac{2m}{\hbar^2}\langle\Theta_i|[\hat{\mathcal{H}}-E]\Theta_j\rangle_{\mathfrak{V}}. \tag{6.4}$$

A stationary value of the functional (6.3) with respect to independent variations in components of $\overline{\mathsf{c}}^\dagger$ and $\overline{\mathsf{c}}'$ is an approximate value of the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}$; hereafter this stationary value will be denoted $(\Phi|\hat{\tilde{\mathcal{R}}}\Phi')_{\mathfrak{S}}$. Thus

$$(\Phi|\hat{\tilde{\mathcal{R}}}\Phi')_{\mathfrak{S}} = \operatorname*{stat}_{\bar{\mathsf{c}}^\dagger,\bar{\mathsf{c}}'} \{\mathsf{f}^\dagger\bar{\mathsf{c}}' + \bar{\mathsf{c}}^\dagger\mathsf{f}' - \bar{\mathsf{c}}^\dagger\mathsf{S}\bar{\mathsf{c}}'\}. \tag{6.5}$$

The yet unknown vectors $\bar{\mathsf{c}}^\dagger$ and $\bar{\mathsf{c}}'$ for which the functional (6.3) is stationary will be denoted by $\tilde{\mathsf{c}}^\dagger$ and $\tilde{\mathsf{c}}'$, respectively. The first variation of Eq. (6.3) due to infinitesimal variations of $\bar{\mathsf{c}}^\dagger$ and $\bar{\mathsf{c}}'$ around $\tilde{\mathsf{c}}^\dagger$ and $\tilde{\mathsf{c}}'$ is

$$\delta F[\mathsf{f}^\dagger,\mathsf{f}';\tilde{\mathsf{c}}^\dagger,\tilde{\mathsf{c}}'] = [\mathsf{f}^\dagger - \tilde{\mathsf{c}}^\dagger\mathsf{S}]\delta\mathsf{c}' + \delta\mathsf{c}^\dagger[\mathsf{f}' - \mathsf{S}\tilde{\mathsf{c}}']. \tag{6.6}$$

A sufficient condition for vanishing of this first variation is

$$\mathsf{f}^\dagger - \tilde{\mathsf{c}}^\dagger\mathsf{S} = 0, \quad \mathsf{f}' - \mathsf{S}\tilde{\mathsf{c}}' = 0; \tag{6.7}$$

hence it follows that

$$\tilde{\mathsf{c}}^\dagger = \mathsf{f}^\dagger\mathsf{S}^{-1}, \quad \tilde{\mathsf{c}}' = \mathsf{S}^{-1}\mathsf{f}'. \tag{6.8}$$

Since the matrix S is the function of energy [cf. Eq. (6.4)], the optimal vectors $\tilde{\mathsf{c}}^\dagger$ and $\tilde{\mathsf{c}}'$ will also be energy dependent.

We now substitute the optimal vectors $\tilde{\mathsf{c}}^\dagger$ and $\tilde{\mathsf{c}}'$ for $\bar{\mathsf{c}}^\dagger$ and $\bar{\mathsf{c}}'$ into Eq. (6.5) and, after making use of Eq. (6.1), arrive at the following estimate of the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}$:

$$(\Phi|\hat{\tilde{\mathcal{R}}}\Phi')_{\mathfrak{S}} = \mathsf{f}^\dagger\mathsf{S}^{-1}\mathsf{f}' = \sum_{i,j=1}^{n} (\Phi|\Theta_i)_{\mathfrak{S}}[\mathsf{S}^{-1}]_{ij}(\Theta_j|\Phi')_{\mathfrak{S}}. \tag{6.9}$$

Since the functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ are arbitrary functions from $\mathcal{A}_{\mathfrak{S}}(E)$, Eq. (6.9) defines a Hermitian integral operator $\hat{\tilde{\mathcal{R}}}(E)$ with the kernel

$$\tilde{\mathcal{R}}(E,\varrho,\varrho') = \sum_{i,j=1}^{n} \Theta_i(\varrho)[\mathsf{S}^{-1}(E)]_{ij}\Theta_j^\dagger(\varrho') \tag{6.10}$$

approximating the kernel of the operator $\hat{\mathcal{R}}(E)$. It is interesting to notice that one also arrives at Eqs. (6.9) and (6.10) using the functional from the principle (5.12). With a suitable change of the variational basis, expansion (6.10) may be transformed to a simpler form. To show this, let us rewrite the matrix $\mathsf{S}(E)$ as

$$\mathsf{S}(E) = \frac{2m}{\hbar^2}[\mathsf{Y} - E\mathsf{O}], \tag{6.11}$$

where Y and O are Hermitian $n\times n$ matrices with elements

$$Y_{ij} = \frac{\hbar^2}{2m}(\Theta_i|\nabla_n\Theta_j)_{\mathfrak{S}} + \langle\Theta_i|\hat{\mathcal{H}}\Theta_j\rangle_{\mathfrak{V}} \tag{6.12}$$

and

$$O_{ij} = \langle\Theta_i|\Theta_j\rangle_{\mathfrak{V}}, \tag{6.13}$$

respectively. The matrix O is the Gram matrix for the set $\{\Theta_i(\mathfrak{r})\}$, and therefore it is non-negative definite. Now consider a generalized matrix eigenvalue problem

$$\mathsf{Y}\mathsf{u}_k = \mathcal{E}_k\mathsf{O}\mathsf{u}_k, \tag{6.14}$$

in which $\mathcal{E}_k$ is the kth eigenvalue and u_k is an associated eigenvector with elements $\{u_{ik}\}$, $(i=1,2,\ldots,n)$. Provided the matrices Y and O are nonsingular, problem (6.14) has exactly n solutions. Because of the Hermiticity of Y and O, the eigenvalues $\{\mathcal{E}_k\}$ are real and eigenvectors corresponding to different eigenvalues are mutually orthogonal in the sense of

$$\mathsf{u}_k^\dagger\mathsf{O}\mathsf{u}_l = 0 \quad (\mathcal{E}_k \neq \mathcal{E}_l). \tag{6.15}$$

Further, since eigenvectors associated with degenerate eigenvalues (if there are any) may always be orthogonalized, and since all eigenvectors may be normalized conveniently, henceforth we shall assume that

$$\mathsf{u}_k^\dagger\mathsf{O}\mathsf{u}_l = \delta_{kl} \quad (k,l=1,2,\ldots,n). \tag{6.16}$$

The eigenvectors $\{\mathsf{u}_k\}$ may be collected in a square $n\times n$ matrix U such that u_k is its kth column. Then from Eqs. (6.14) and (6.16) we deduce

$$\mathsf{Y}\mathsf{U} = \mathsf{O}\mathsf{U}\boldsymbol{\mathcal{E}}, \tag{6.17}$$

$$\mathsf{U}^\dagger\mathsf{O}\mathsf{U} = \mathsf{I}, \tag{6.18}$$

where $\boldsymbol{\mathcal{E}}$ is a diagonal $n\times n$ matrix with elements $\{\mathcal{E}_{kl} = \mathcal{E}_k\delta_{kl}\}$, while I is the unit $n\times n$ matrix. Equations (6.17) and (6.18) imply

$$\mathsf{U}^\dagger\mathsf{Y}\mathsf{U} = \boldsymbol{\mathcal{E}} \tag{6.19}$$

while Eqs. (6.11), (6.18), and (6.19) yield

$$\mathsf{U}^\dagger\mathsf{S}(E)\mathsf{U} = \frac{2m}{\hbar^2}[\boldsymbol{\mathcal{E}} - E\mathsf{I}]. \tag{6.20}$$

Hence, after simple manipulations, we arrive at

$$\mathsf{S}^{-1}(E) = \frac{\hbar^2}{2m}\mathsf{U}[\boldsymbol{\mathcal{E}} - E\mathsf{I}]^{-1}\mathsf{U}^\dagger. \tag{6.21}$$

Equation (6.21) shows that the ijth element of the matrix $\mathsf{S}^{-1}(E)$ is

$$[\mathsf{S}^{-1}(E)]_{ij} = \frac{\hbar^2}{2m}\sum_{k=1}^{n}\frac{u_{ik}u_{jk}^*}{\mathcal{E}_k - E}. \tag{6.22}$$

Making use of this result in Eq. (6.10) and defining the functions

$$\Lambda_k(\mathfrak{r}) = \sum_{i=1}^{n} u_{ik}\Theta_i(\mathfrak{r}) \quad (k=1,2,\ldots,n) \tag{6.23}$$

with the orthonormality property

$$\langle\Lambda_k|\Lambda_l\rangle_{\mathfrak{V}} = \delta_{kl}, \tag{6.24}$$

following from the matrix relation (6.18), we obtain

$$\tilde{\mathcal{R}}(E,\varrho,\varrho') = \frac{\hbar^2}{2m}\sum_{k=1}^{n}\frac{\Lambda_k(\varrho)\Lambda_k^\dagger(\varrho')}{\mathcal{E}_k - E}. \tag{6.25}$$

Notice that since, in general, the hypersurface functions $\{\Lambda_k(\varrho)\}$ are not orthogonal under the scalar product $(|)_{\mathfrak{S}}$, Eq. (6.25) is *not* the spectral expansion of the kernel of $\hat{\tilde{\mathcal{R}}}(E)$ [cf. Sec. VI D].

B. Estimates of matrix elements of $\hat{\mathcal{B}}(E)$

Considerations analogous to those presented in Sec. VI A lead to variational estimates of matrix elements and the kernel of the operator $\hat{\mathcal{B}}(E)$. Substitution of the trial functions (6.1) into the functional

$$F[\Phi,\Phi';\overline{\Psi},\overline{\Psi}'] = (\Phi|\nabla_n\overline{\Psi}')_{\mathfrak{S}} + (\nabla_n\overline{\Psi}|\Phi')_{\mathfrak{S}} - (\nabla_n\overline{\Psi}|\overline{\Psi}')_{\mathfrak{S}} + \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}'\rangle_{\mathfrak{V}} \tag{6.26}$$

[cf. the right side of Eq. (5.3)] gives

$$F[\mathsf{g}^\dagger,\mathsf{g}';\overline{\mathsf{c}}^\dagger,\overline{\mathsf{c}}'] = \mathsf{g}^\dagger\overline{\mathsf{c}}' + \overline{\mathsf{c}}^\dagger\mathsf{g}' - \overline{\mathsf{c}}^\dagger\mathsf{T}\overline{\mathsf{c}}', \tag{6.27}$$

where $\mathsf{g}^\dagger$ is an n-component row matrix with elements $\{g_i^* = (\Phi|\nabla_n\Theta_i)_{\mathfrak{S}}\}$, g' is an n-component column matrix with elements $\{g_i' = (\nabla_n\Theta_i|\Phi')_{\mathfrak{S}}\}$, and $\mathsf{T}(E)$ is a Hermitian $n\times n$ matrix with elements

$$T_{ij}(E) = (\nabla_n\Theta_i|\Theta_j)_{\mathfrak{S}} - \frac{2m}{\hbar^2}\langle\Theta_i|[\hat{\mathcal{H}}-E]\Theta_j\rangle_{\mathfrak{V}}. \tag{6.28}$$

A stationary value of the functional (6.27) with respect to infinitesimal variations of components of $\overline{\mathsf{c}}^\dagger$ and $\overline{\mathsf{c}}'$ is a matrix element, between the functions $\Phi(\varrho)$ and $\Phi'(\varrho)$, of the operator $\hat{\tilde{\mathcal{B}}}(E)$ being a variational estimate of $\hat{\mathcal{B}}(E)$:

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}} = \operatorname*{stat}_{\overline{\mathsf{c}}^\dagger,\overline{\mathsf{c}}'}\{\mathsf{g}^\dagger\overline{\mathsf{c}}' + \overline{\mathsf{c}}^\dagger\mathsf{g}' - \overline{\mathsf{c}}^\dagger\mathsf{T}\overline{\mathsf{c}}'\}. \tag{6.29}$$

These vectors $\overline{\mathsf{c}}^\dagger$ and $\overline{\mathsf{c}}'$ for which the functional (6.27) is stationary will be denoted by $\tilde{\mathsf{c}}^\dagger$ and $\tilde{\mathsf{c}}'$. The stationary condition

$$\delta F[\mathsf{g}^\dagger,\mathsf{g}';\tilde{\mathsf{c}}^\dagger,\tilde{\mathsf{c}}'] = 0 \tag{6.30}$$

leads to the relations

$$\tilde{\mathsf{c}}^\dagger = \mathsf{g}^\dagger\mathsf{T}^{-1}, \quad \tilde{\mathsf{c}}' = \mathsf{T}^{-1}\mathsf{g}'. \tag{6.31}$$

On using this result in Eq. (6.29), we obtain the following estimates of the matrix element $(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}$:

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}} = \mathsf{g}^\dagger\mathsf{T}^{-1}\mathsf{g}' = \sum_{i,j=1}^{n}(\Phi|\nabla_n\Theta_i)_{\mathfrak{S}}[\mathsf{T}^{-1}]_{ij}(\nabla_n\Theta_j|\Phi')_{\mathfrak{S}}; \tag{6.32}$$

and those of the integral kernel $\mathcal{B}(E,\varrho,\varrho')$:

$$\tilde{\mathcal{B}}(E,\varrho,\varrho') = \sum_{i,j=1}^{n}\nabla_n\Theta_i(\varrho)[\mathsf{T}^{-1}(E)]_{ij}\nabla_n\Theta_j^\dagger(\varrho'). \tag{6.33}$$

It is evident that kernel (6.33) is Hermitian. Equations (6.32) and (6.33) are also obtained if one uses the trial functions (6.1) in the variational principle (5.11).

Let Z be a nonsingular Hermitian $n\times n$ matrix with elements

$$Z_{ij} = -\frac{\hbar^2}{2m}(\nabla_n\Theta_i|\Theta_j)_{\mathfrak{S}} + \langle\Theta_i|\hat{\mathcal{H}}\Theta_j\rangle_{\mathfrak{V}}, \tag{6.34}$$

and let O be a nonsingular $n\times n$ matrix defined by Eq. (6.13). Then

$$\mathsf{T}(E) = -\frac{2m}{\hbar^2}[\mathsf{Z}-E\mathsf{O}]. \tag{6.35}$$

We denote by $\boldsymbol{\mathcal{E}}$ the spectral matrix (with elements $\{\mathcal{E}_k\delta_{kl}\}$) and by V the modal matrix (with elements $\{v_{ik}\}$) for a matrix eigenvalue problem

$$\mathsf{ZV} = \mathsf{OV}\boldsymbol{\mathcal{E}}, \tag{6.36}$$

and assume that

$$\mathsf{V}^\dagger\mathsf{OV} = \mathsf{I}. \tag{6.37}$$

After a few movements similar to those presented at the end of Sec. VI A, we arrive at

$$\mathsf{T}^{-1}(E) = -\frac{\hbar^2}{2m}\mathsf{V}[\boldsymbol{\mathcal{E}}-E\mathsf{I}]^{-1}\mathsf{V}^\dagger, \tag{6.38}$$

which is equivalent to the statement that the ijth element of $\mathsf{T}^{-1}(E)$ is

$$[\mathsf{T}^{-1}(E)]_{ij} = -\frac{\hbar^2}{2m}\sum_{k=1}^{n}\frac{v_{ik}v_{jk}^*}{\mathcal{E}_k-E}. \tag{6.39}$$

Denoting

$$\Upsilon_k(\mathfrak{r}) = \sum_{i=1}^{n} v_{ik}\Theta_i(\mathfrak{r}) \quad (k=1,2,\ldots,n), \tag{6.40}$$

and combining result (6.39) with Eq. (6.33), we obtain

$$\tilde{\mathcal{B}}(E,\varrho,\varrho') = -\frac{\hbar^2}{2m}\sum_{k=1}^{n}\frac{\nabla_n\Upsilon_k(\varrho)\nabla_n\Upsilon_k^\dagger(\varrho')}{\mathcal{E}_k-E}. \tag{6.41}$$

It is to be mentioned that Eq. (6.41) is *not* the spectral expansion of the kernel $\tilde{\mathcal{B}}(E,\varrho,\varrho')$ (cf. the remark concluding the preceding subsection; see also Sec. VI C).

C. Estimates of eigenvalues of $\hat{\mathcal{B}}(E)$

The linear trial functions may also be used for estimating eigenvalues of $\hat{\mathcal{B}}(E)$. Choosing, in the functional

$$F[\bar{\Psi}]=\frac{(\bar{\Psi}|\nabla_n\bar{\Psi})_{\mathfrak{S}}}{(\bar{\Psi}|\bar{\Psi})_{\mathfrak{S}}}+\frac{2m}{\hbar^2}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}}-E]\bar{\Psi}\rangle_{\mathfrak{V}}}{(\bar{\Psi}|\bar{\Psi})_{\mathfrak{S}}}, \quad (6.42)$$

[cf. the right-hand side of the principle (5.1)] the trial function $\bar{\Psi}(\mathfrak{r})$ in the form

$$\bar{\Psi}(\mathfrak{r})=\sum_{i=1}^{n}\bar{a}_i\Theta_i(\mathfrak{r}) \quad (\Theta_i(\mathfrak{r})\in\mathcal{A}''_{\mathfrak{V}}) \quad (6.43)$$

leads to the functional

$$F[\bar{\mathbf{a}}^\dagger,\bar{\mathbf{a}}]=\frac{\bar{\mathbf{a}}^\dagger\mathsf{S}\bar{\mathbf{a}}}{\bar{\mathbf{a}}^\dagger\mathsf{M}\bar{\mathbf{a}}}, \quad (6.44)$$

in which $\bar{\mathbf{a}}$ is an n-component column matrix with elements $\{\bar{a}_i\}$, $\bar{\mathbf{a}}^\dagger$ is an n-component row matrix with elements $\{\bar{a}_i^*\}$, $\mathsf{S}\equiv\mathsf{S}(E)$ is the Hermitian $n\times n$ matrix defined by Eq. (6.4), and M is a Hermitian $n\times n$ overlap matrix with elements

$$M_{ij}=(\Theta_i|\Theta_j)_{\mathfrak{S}}. \quad (6.45)$$

We shall denote by $\tilde{\mathbf{a}}$ and $\tilde{\mathbf{a}}^\dagger$ these vectors $\bar{\mathbf{a}}$ and $\bar{\mathbf{a}}^\dagger$ for which the functional (6.44) is stationary with respect to variations in their components, i.e.,

$$\delta F[\tilde{\mathbf{a}}^\dagger,\tilde{\mathbf{a}}]=0. \quad (6.46)$$

The corresponding stationary values, approximating eigenvalues of $\hat{\mathcal{B}}(E)$, will be denoted by $\tilde{b}$; one has

$$\tilde{b}=\frac{\tilde{\mathbf{a}}^\dagger\mathsf{S}\tilde{\mathbf{a}}}{\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}}}. \quad (6.47)$$

From Eq. (6.44) one finds that the first variation of the functional $F[\bar{\mathbf{a}}^\dagger,\bar{\mathbf{a}}]$ due to infinitesimal variations of $\bar{\mathbf{a}}^\dagger$ and $\bar{\mathbf{a}}$ around $\tilde{\mathbf{a}}^\dagger$ and $\tilde{\mathbf{a}}$, respectively, is

$$\delta F[\tilde{\mathbf{a}}^\dagger,\tilde{\mathbf{a}}]=\delta\mathbf{a}^\dagger\frac{(\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}})\mathsf{S}\tilde{\mathbf{a}}-(\tilde{\mathbf{a}}^\dagger\mathsf{S}\tilde{\mathbf{a}})\mathsf{M}\tilde{\mathbf{a}}}{(\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}})^2}+\frac{(\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}})\tilde{\mathbf{a}}^\dagger\mathsf{S}-(\tilde{\mathbf{a}}^\dagger\mathsf{S}\tilde{\mathbf{a}})\tilde{\mathbf{a}}^\dagger\mathsf{M}}{(\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}})^2}\delta\mathbf{a}. \quad (6.48)$$

It is seen that conditions for $F[\bar{\mathbf{a}}^\dagger,\bar{\mathbf{a}}]$ to be stationary at $\tilde{\mathbf{a}}^\dagger$ and $\tilde{\mathbf{a}}$ are

$$\mathsf{S}\tilde{\mathbf{a}}=\frac{\tilde{\mathbf{a}}^\dagger\mathsf{S}\tilde{\mathbf{a}}}{\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}}}\mathsf{M}\tilde{\mathbf{a}}, \quad \tilde{\mathbf{a}}^\dagger\mathsf{S}=\frac{\tilde{\mathbf{a}}^\dagger\mathsf{S}\tilde{\mathbf{a}}}{\tilde{\mathbf{a}}^\dagger\mathsf{M}\tilde{\mathbf{a}}}\tilde{\mathbf{a}}^\dagger\mathsf{M}; \quad (6.49)$$

hence we conclude that $\tilde{b}$ is an eigenvalue while $\tilde{\mathbf{a}}$ and $\tilde{\mathbf{a}}^\dagger$ are, respectively, corresponding right and left eigenvectors of the generalized matrix eigenvalue problems

$$\mathsf{S}\tilde{\mathbf{a}}=\tilde{b}\mathsf{M}\tilde{\mathbf{a}}, \quad \tilde{\mathbf{a}}^\dagger\mathsf{S}=\tilde{b}\tilde{\mathbf{a}}^\dagger\mathsf{M}. \quad (6.50)$$

If the matrix S is nonsingular, the number of solutions to these eigenproblems will be equal to the rank of the matrix M which, in general, will be *less* than the number n of coordinate functions used (cf. Refs. [16], [21]). We note also that since the matrix S is the function of energy [cf. Eq. (6.4)], the eigenvectors $\{\tilde{\mathbf{a}}_k\}$ and the eigenvalues $\{\tilde{b}_k\}$ will be energy dependent.

We observe that the Hermiticity properties of $\mathsf{S}(E)$ and M imply that any two eigenvectors $\tilde{\mathbf{a}}_k(E)$ and $\tilde{\mathbf{a}}_l(E)$ [with elements $\{\tilde{a}_{ik}(E)\}$ and $\{\tilde{a}_{il}(E)\}$, respectively] of the problem (6.50), associated with different eigenvalues $\tilde{b}_k(E)$ and $\tilde{b}_l(E)$, respectively, are orthogonal in the sense of

$$\tilde{\mathbf{a}}_k^\dagger(E)\mathsf{M}\tilde{\mathbf{a}}_l(E)=0 \quad (\tilde{b}_k(E)\neq\tilde{b}_l(E)). \quad (6.51)$$

In what follows, we shall assume that eigenvectors corresponding to degenerate eigenvalues (if there are any) have also been orthogonalized and that all eigenvectors have been normalized so that for any pair of eigenvectors one has

$$\tilde{\mathbf{a}}_k^\dagger(E)\mathsf{M}\tilde{\mathbf{a}}_l(E)=\delta_{kl}. \quad (6.52)$$

We shall use the symbols $\{\tilde{\Psi}_k(E,\mathfrak{r})\}$ to denote functions of the form (6.43) with the expansion coefficients being components of the eigenvectors $\{\tilde{\mathbf{a}}_k(E)\}$:

$$\tilde{\Psi}_k(E,\mathfrak{r})=\sum_{i=1}^{n}\tilde{a}_{ik}(E)\Theta_i(\mathfrak{r}) \quad (k=1,2,\ldots,\text{rank }\mathsf{M}). \quad (6.53)$$

Then it is evident that the matrix relation (6.51) implies the orthonormality relation

$$(\tilde{\Psi}_k|\tilde{\Psi}_l)_{\mathfrak{S}}=\delta_{kl} \quad (6.54)$$

for the functions $\{\tilde{\Psi}_k(E,\varrho)\}$ [cf. Eq. (3.16)].

We have found that the set of the functions $\{\tilde{\Psi}_k(E,\mathfrak{r})\}$, $(k=1,2,\ldots,\text{rank }\mathsf{M})$, defined by Eq. (6.53), is ideally suited as a basis for variational approximation of matrix elements and the kernel of the operator $\hat{\mathcal{R}}(E)$. To show this, let us construct trial functions of the form

$$\bar{\Psi}(\mathfrak{r})=\sum_{k=1}^{\text{rank }\mathsf{M}}\bar{c}_k\tilde{\Psi}_k(E,\mathfrak{r}), \quad \bar{\Psi}'(\mathfrak{r})=\sum_{k=1}^{\text{rank }\mathsf{M}}\bar{c}'_k\tilde{\Psi}'_k(E,\mathfrak{r}), \quad (6.55)$$

where $\{\bar{c}_k\}$ and $\{\bar{c}'_k\}$ are variational parameters. Proceeding along the lines of Sec. VI A, we obtain

$$(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}=\sum_{k,l=1}^{\text{rank }\mathsf{M}}(\Phi|\tilde{\Psi}_k)_{\mathfrak{S}}[\tilde{\mathsf{S}}^{-1}]_{kl}(\tilde{\Psi}_l|\Phi')_{\mathfrak{S}}, \quad (6.56)$$

where $\tilde{\mathsf{S}}(E)$ is the square Hermitian matrix of dimensions $\text{rank }\mathsf{M}\times\text{rank }\mathsf{M}$ with elements

$$\tilde{S}_{kl}(E)=(\tilde{\Psi}_k|\nabla_n\tilde{\Psi}_l)_{\mathfrak{S}}+\frac{2m}{\hbar^2}\langle\tilde{\Psi}_k|[\hat{\mathcal{H}}-E]\tilde{\Psi}_l\rangle_{\mathfrak{V}}. \quad (6.57)$$

Upon making use of Eqs. (6.53) and (6.4), Eq. (6.57) may be rewritten in the form

$$\tilde{S}_{kl}(E)=\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{S}(E)\tilde{\mathbf{a}}_l(E). \tag{6.58}$$

The right side of Eq. (6.58) may be simplified further if one takes into account either of the two eigenvalue equations (6.50) and the orthonormality condition (6.52). This results in

$$\tilde{S}_{kl}(E)=\tilde{b}_k(E)\,\delta_{kl}, \tag{6.59}$$

which implies that the matrix $\tilde{\mathsf{S}}^{-1}(E)$ is diagonal and that its diagonal matrix elements are reciprocals of eigenvalues of the problem (6.50). From Eqs. (6.56), (6.59), and (6.53), we obtain

$$\begin{aligned}(\Phi|\hat{\tilde{\mathcal{R}}}\Phi')_{\mathfrak{S}}&=\sum_{k=1}^{\text{rank }\mathsf{M}}(\Phi|\tilde{\Psi}_k)_{\mathfrak{S}}\tilde{b}_k^{-1}(\tilde{\Psi}_k|\Phi')_{\mathfrak{S}}\\&=\sum_{i,j=1}^{n}(\Phi|\Theta_i)_{\mathfrak{S}}\left[\sum_{k=1}^{\text{rank }\mathsf{M}}\tilde{a}_{ik}\tilde{b}_k^{-1}\tilde{a}_{jk}^{*}\right](\Theta_j|\Phi')_{\mathfrak{S}}.\end{aligned} \tag{6.60}$$

Since the functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ are arbitrary, from Eq. (6.60) we deduce the spectral expansion [cf. Eq. (3.34)]

$$\begin{aligned}\tilde{\mathcal{R}}(E,\varrho,\varrho')&=\sum_{k=1}^{\text{rank }\mathsf{M}}\tilde{\Psi}_k(E,\varrho)\tilde{b}_k^{-1}(E)\tilde{\Psi}_k^{\dagger}(E,\varrho')\\&=\sum_{i,j=1}^{n}\Theta_i(\varrho)\\&\quad\times\left[\sum_{k=1}^{\text{rank }\mathsf{M}}\tilde{a}_{ik}(E)\tilde{b}_k^{-1}(E)\tilde{a}_{jk}^{*}(E)\right]\Theta_j^{\dagger}(\varrho').\end{aligned} \tag{6.61}$$

Expansion (6.61) and the orthonormality relation (6.54) show that the numbers $\{\tilde{b}_k^{-1}(E)\}$, $(k=1,2,\ldots,\text{rank}\,\mathsf{M})$, are eigenvalues of the Hermitian operator $\hat{\tilde{\mathcal{R}}}(E)$ with the kernel $\tilde{\mathcal{R}}(E,\varrho,\varrho')$ and the functions $\{\tilde{\Psi}_k(E,\varrho)\}$ are normalized eigenfunctions of this operator. The operator $\hat{\tilde{\mathcal{R}}}(E)$ is the variational estimate of the operator $\hat{\mathcal{R}}(E)$.

It is also natural to use the trial functions (6.43) to approximate matrix elements of $\hat{\mathcal{B}}(E)$ by employing the procedure outlined in Sec. VI B. Denoting the resulting estimate of $(\Phi|\hat{\mathcal{B}}\Phi')_{\mathfrak{S}}$ by $(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}}$ we obtain

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}}=\sum_{k,l=1}^{\text{rank }\mathsf{M}}(\Phi|\nabla_n\tilde{\Psi}_k)_{\mathfrak{S}}[\tilde{\mathsf{T}}^{-1}]_{kl}(\nabla_n\tilde{\Psi}_l|\Phi')_{\mathfrak{S}}, \tag{6.62}$$

where $\tilde{\mathsf{T}}\equiv\tilde{\mathsf{T}}(E)$ is a Hermitian rank $\mathsf{M}\times$rank M matrix with elements

$$\tilde{T}_{kl}(E)=(\nabla_n\tilde{\Psi}_k|\tilde{\Psi}_l)_{\mathfrak{S}}-\frac{2m}{\hbar^2}\langle\tilde{\Psi}_k|[\hat{\mathcal{H}}-E]\tilde{\Psi}_l\rangle_{\mathfrak{V}}, \tag{6.63}$$

which, after making use of Eq. (6.53), may be rewritten as

$$\tilde{T}_{kl}(E)=\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{T}(E)\tilde{\mathbf{a}}_l(E), \tag{6.64}$$

with the Hermitian $n\times n$ matrix $\mathsf{T}(E)$ defined by Eq. (6.28). It is seen that, as opposed to $\tilde{\mathsf{S}}(E)$, the matrix $\tilde{\mathsf{T}}(E)$ is *not* diagonal. Therefore, the variational approximations

$$\begin{aligned}(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}}&=\sum_{k,l=1}^{\text{rank }\mathsf{M}}(\Phi|\nabla_n\tilde{\Psi}_k)_{\mathfrak{S}}[\tilde{\mathsf{T}}^{-1}]_{kl}(\nabla_n\tilde{\Psi}_l|\Phi')_{\mathfrak{S}}\\&=\sum_{i,j=1}^{n}(\Phi|\nabla_n\Theta_i)_{\mathfrak{S}}\left[\sum_{k,l=1}^{\text{rank }\mathsf{M}}\tilde{a}_{ik}[\tilde{\mathsf{T}}^{-1}]_{kl}\tilde{a}_{jl}^{*}\right]\\&\quad\times(\nabla_n\Theta_j|\Phi')_{\mathfrak{S}}\end{aligned} \tag{6.65}$$

and

$$\begin{aligned}\tilde{\mathcal{B}}(E,\varrho,\varrho')&=\sum_{k,l=1}^{\text{rank }\mathsf{M}}\nabla_n\tilde{\Psi}_k(E,\varrho)[\tilde{\mathsf{T}}^{-1}(E)]_{kl}\nabla_n\tilde{\Psi}_l^{\dagger}(E,\varrho')\\&=\sum_{i,j=1}^{n}\nabla_n\Theta_i(\varrho)\\&\quad\times\left[\sum_{k,l=1}^{\text{rank }\mathsf{M}}\tilde{a}_{ik}(E)[\tilde{\mathsf{T}}^{-1}(E)]_{kl}\tilde{a}_{jl}^{*}(E)\right]\nabla_n\Theta_j^{\dagger}(\varrho')\end{aligned} \tag{6.66}$$

will be of less practical value than their counterparts (6.60) and (6.61).

It is worth noticing that, in analogy with the spectral expansion (3.18), one may introduce the operator $\hat{\tilde{\mathfrak{B}}}(E)$ with the kernel

$$\begin{aligned}&\tilde{\mathfrak{B}}(E,\varrho,\varrho')\\&\quad=\sum_{k=1}^{\text{rank }\mathsf{M}}\tilde{\Psi}_k(E,\varrho)\tilde{b}_k(E)\tilde{\Psi}_k^{\dagger}(E,\varrho')\\&\quad=\sum_{i,j=1}^{n}\Theta_i(\varrho)\left[\sum_{k=1}^{\text{rank }\mathsf{M}}\tilde{a}_{ik}(E)\tilde{b}_k(E)\tilde{a}_{jk}^{*}(E)\right]\Theta_j^{*}(\varrho')\end{aligned} \tag{6.67}$$

as an estimate of $\hat{\mathcal{B}}(E)$. It is seen from the definitions (6.61) and (6.67) and from the orthonormality relation (6.54) that the operators $\hat{\tilde{\mathfrak{B}}}(E)$ and $\hat{\tilde{\mathcal{R}}}(E)$ are reciprocal in the sense that

$$\hat{\tilde{\mathfrak{B}}}(E)\hat{\tilde{\mathcal{R}}}(E)=\hat{\tilde{\mathcal{R}}}(E)\hat{\tilde{\mathfrak{B}}}(E)=\hat{\tilde{\mathcal{A}}}_{\mathfrak{S}}(E), \tag{6.68}$$

where the operator $\hat{\tilde{\mathcal{A}}}_{\mathfrak{S}}(E)$ with the kernel [cf. Eq. (3.23)]

$$\tilde{\mathcal{A}}_{\mathfrak{S}}(E,\varrho,\varrho')=\sum_{k=1}^{\text{rank }M}\tilde{\Psi}_k(E,\varrho)\tilde{\Psi}_k^{\dagger}(E,\varrho') \tag{6.69}$$

is the projector on the subspace of $\mathcal{A}_{\mathfrak{S}}(E)$ spanned by the approximate eigenfunctions $\{\tilde{\Psi}_k(E,\varrho)\}$, $(k=1,2,\ldots,\text{rank}$

M). It should be pointed out, however, that, as opposed to $\hat{\tilde{\mathcal{B}}}(E)$, the operator $\hat{\tilde{\mathfrak{B}}}(E)$ is *not* the *variational* estimate of $\hat{\mathcal{B}}(E)$.

D. Estimates of eigenvalues of $\hat{\mathcal{R}}(E)$

Finally, we shall use the Rayleigh-Ritz trial functions (6.43) in the functional

$$F[\overline{\Psi}]=\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}} \tag{6.70}$$

[cf. the right side of Eq. (5.2)] to find approximations to eigenvalues of $\hat{\mathcal{R}}(E)$. Substitution of Eq. (6.43) into the functional (6.70) transforms the latter to the form

$$F[\overline{\mathbf{a}}^{\dagger},\overline{\mathbf{a}}]=\frac{\overline{\mathbf{a}}^{\dagger}\mathsf{T}\overline{\mathbf{a}}}{\overline{\mathbf{a}}^{\dagger}\mathsf{N}\overline{\mathbf{a}}}. \tag{6.71}$$

Here $\overline{\mathbf{a}}$ and $\overline{\mathbf{a}}^{\dagger}$ are defined as in Eq. (6.44), $\mathsf{T}\equiv\mathsf{T}(E)$ is the Hermitian $n\times n$ matrix defined by Eq. (6.28) while N is a Hermitian $n\times n$ matrix with elements

$$N_{ij}=(\nabla_n\Theta_i|\nabla_n\Theta_j)_{\mathfrak{S}}. \tag{6.72}$$

Denoting by $\tilde{\mathbf{a}}$ and $\tilde{\mathbf{a}}^{\dagger}$ these vectors $\overline{\mathbf{a}}$ and $\overline{\mathbf{a}}^{\dagger}$ for which

$$\delta F[\tilde{\mathbf{a}}^{\dagger},\tilde{\mathbf{a}}]=0, \tag{6.73}$$

and defining the real number

$$\widetilde{b^{-1}}=\frac{\tilde{\mathbf{a}}^{\dagger}\mathsf{T}\tilde{\mathbf{a}}}{\tilde{\mathbf{a}}^{\dagger}\mathsf{N}\tilde{\mathbf{a}}}, \tag{6.74}$$

from Eqs. (6.71) and (6.73) we find that $\widetilde{b^{-1}}$, $\tilde{\mathbf{a}}$, and $\tilde{\mathbf{a}}^{\dagger}$ are solutions to the matrix eigenvalue problems

$$\mathsf{T}\tilde{\mathbf{a}}=\widetilde{b^{-1}}\mathsf{N}\tilde{\mathbf{a}},\quad \tilde{\mathbf{a}}^{\dagger}\mathsf{T}=\widetilde{b^{-1}}\tilde{\mathbf{a}}^{\dagger}\mathsf{N}. \tag{6.75}$$

If T is nonsingular, the number of nontrivial solutions to these eigenproblems equals to the rank of N.

It should be clearly stated here that even if the basis functions $\{\Theta_i(\mathfrak{r})\}$ used for constructing the trial functions $\overline{\Psi}(\mathfrak{r})$ substituted to the functionals (6.42) and (6.70) are the same, in general one has rank $\mathsf{N}\neq$ rank M. Moreover, if $\widetilde{b_k^{-1}}(E)$ is an eigenvalue of the problem (6.75) approximating some particular eigenvalue $b_k^{-1}(E)$ of the operator $\hat{\mathcal{R}}(E)$ and if $\tilde{b}_k(E)$ is an eigenvalue of the problem (6.50) approximating the eigenvalue $b_k(E)$ of $\hat{\mathcal{B}}(E)$, in general, one finds

$$\widetilde{b_k^{-1}}(E)\neq\tilde{b}_k^{-1}(E). \tag{6.76}$$

Similarly, the eigenvectors $\tilde{\mathbf{a}}_k(E)$ [and $\tilde{\mathbf{a}}_k^{\dagger}(E)$] of the problems (6.50) and (6.75) associated with eigenvalues $\tilde{b}_k(E)$ and $\widetilde{b_k^{-1}}(E)$, respectively, in general will be different though we use the same symbols to denote them.

The Hermiticity of $\mathsf{T}(E)$ and N implies that eigenvectors of the problem (6.75) associated with different eigenvalues are orthogonal in the sense that

$$\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{N}\tilde{\mathbf{a}}_l(E)=0\quad(\widetilde{b_k^{-1}}(E)\neq\widetilde{b_l^{-1}}(E)). \tag{6.77}$$

In what follows, we shall also assume that eigenvectors associated with degenerate eigenvalues (if there are any) have also been orthogonalized, and that all eigenvectors have been normalized so that

$$\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{N}\tilde{\mathbf{a}}_l(E)=[\widetilde{b_k^{-1}}(E)]^{-2}\delta_{kl}. \tag{6.78}$$

Relation (6.78) implies that the functions

$$\tilde{\Psi}_k(E,\mathfrak{r})=\sum_{i=1}^{n}\tilde{a}_{ik}(E)\Theta_i(\mathfrak{r})\quad(k=1,2,\ldots,\text{rank }\mathsf{N}), \tag{6.79}$$

with the coefficients $\{\tilde{a}_{ik}(E)\}$, being components of the eigenvectors $\{\tilde{\mathbf{a}}_k(E)\}$ of the problem (6.75), satisfy the following orthogonality relation on $\mathfrak{S}$:

$$(\nabla_n\tilde{\Psi}_k|\nabla_n\tilde{\Psi}_l)_{\mathfrak{S}}=[\widetilde{b_k^{-1}}(E)]^{-2}\delta_{kl} \tag{6.80}$$

[cf. the orthogonality relation (3.17)]. On the hypersurface $\mathfrak{S}$, the functions (6.79) approximate eigenfunctions of $\hat{\mathcal{R}}(E)$.

Once the optimal functions (6.79) have been found, their linear combinations of the forms

$$\tilde{\Psi}(\mathfrak{r})=\sum_{k=1}^{\text{rank }\mathsf{N}}\overline{c}_k\tilde{\Psi}_k(E,\mathfrak{r}),\quad \overline{\Psi}'(\mathfrak{r})=\sum_{k=1}^{\text{rank }\mathsf{N}}\overline{c}_k'\tilde{\Psi}_k(E,\mathfrak{r}), \tag{6.81}$$

with the coefficients $\{\overline{c}_k\}$ and $\{\overline{c}_k'\}$ subjected to variations, may be suitably used for construction of the variational approximation of the operator $\hat{\mathcal{B}}(E)$. Utilizing the results of Sec. VI B, we obtain

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')_{\mathfrak{S}}=\sum_{k,l=1}^{\text{rank }\mathsf{N}}(\Phi|\nabla_n\tilde{\Psi}_k)_{\mathfrak{S}}[\underline{\tilde{T}}^{-1}]_{kl}(\nabla_n\tilde{\Psi}_l|\Phi')_{\mathfrak{S}}, \tag{6.82}$$

with $\underline{\tilde{T}}(E)$ being the square Hermitian matrix of dimensions rank $\mathsf{N}\times$ rank N with elements

$$\underline{\tilde{T}}_{kl}(E)=(\nabla_n\tilde{\Psi}_k|\tilde{\Psi}_l)_{\mathfrak{S}}-\frac{2m}{\hbar^2}\langle\tilde{\Psi}_k|[\hat{\mathcal{H}}-E]\tilde{\Psi}_l\rangle_{\mathfrak{V}}. \tag{6.83}$$

[The matrices $\tilde{\mathsf{T}}(E)$ and $\underline{\tilde{T}}(E)$ defined by apparently identical Eqs. (6.63) and (6.83) are, in general, *different* since the approximate eigenfunctions (6.53) and (6.79) differ in number and form.] Upon substituting Eq. (6.79) into Eq. (6.82), the latter becomes

$$\underline{\tilde{T}}_{kl}(E)=\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{T}(E)\tilde{\mathbf{a}}_l(E). \tag{6.84}$$

Then, as a result of any of the eigenvalue problems (6.75) and the orthogonality relation (6.78), the above equation is transformed to the form

$$\tilde{\underline{T}}_{kl}(E)=[\widetilde{b_k^{-1}}(E)]^{-1}\delta_{kl}, \tag{6.85}$$

showing that the matrix $\tilde{\underline{T}}(E)$ is diagonal. Consequently, its inversion is trivial and from Eqs. (6.82) and (6.85), we arrive at

$$\begin{aligned}(\Phi|\hat{\tilde{\underline{\mathcal{B}}}}\Phi')_{\mathfrak{S}}&=\sum_{k=1}^{\text{rank N}}(\Phi|\nabla_n\tilde{\Psi}_k)_{\mathfrak{S}}\widetilde{b_k^{-1}}(\nabla_n\tilde{\Psi}_k|\Phi')_{\mathfrak{S}}\\&=\sum_{i,j=1}^{n}(\Phi|\nabla_n\Theta_i)_{\mathfrak{S}}\left[\sum_{k=1}^{\text{rank N}}\tilde{a}_{ik}\widetilde{b_k^{-1}}\tilde{a}_{jk}^*\right]\\&\quad\times(\nabla_n\Theta_j|\Phi')_{\mathfrak{S}}\end{aligned} \tag{6.86}$$

and [cf. Eq. (3.19)]

$$\begin{aligned}\tilde{\mathcal{B}}(E,\varrho,\varrho')&=\sum_{k=1}^{\text{rank N}}\nabla_n\tilde{\Psi}_k(E,\varrho)\widetilde{b_k^{-1}}(E)\nabla_n\tilde{\Psi}_k^{\dagger}(E,\varrho')\\&=\sum_{i,j=1}^{n}\nabla_n\Theta_i(\varrho)\\&\quad\times\left[\sum_{k=1}^{\text{rank N}}\tilde{a}_{ik}(E)\widetilde{b_k^{-1}}(E)\tilde{a}_{jk}^*(E)\right]\nabla_n\Theta_j^{\dagger}(\varrho').\end{aligned} \tag{6.87}$$

The trial functions (6.81) may also be used for approximating matrix elements and the kernel of $\hat{\mathcal{R}}(E)$. Following the procedure outlined in Sec. VI A, one arrives at the following estimate of $(\Phi|\hat{\mathcal{R}}\Phi')_{\mathfrak{S}}$

$$\begin{aligned}(\Phi|\hat{\tilde{\underline{\mathcal{R}}}}\Phi')_{\mathfrak{S}}&=\sum_{k,l=1}^{\text{rank N}}(\Phi|\tilde{\Psi}_k)_{\mathfrak{S}}[\tilde{\underline{\mathsf{S}}}^{-1}]_{kl}(\tilde{\Psi}_l|\Phi')_{\mathfrak{S}}\\&=\sum_{i,j=1}^{n}(\Phi|\Theta_i)_{\mathfrak{S}}\left[\sum_{k,l=1}^{\text{rank N}}\tilde{a}_{ik}[\tilde{\underline{\mathsf{S}}}^{-1}]_{kl}\tilde{a}_{jl}^*\right]\\&\quad\times(\Theta_j|\Phi')_{\mathfrak{S}},\end{aligned} \tag{6.88}$$

from which the following approximation to the kernel $\mathcal{R}(E,\varrho,\varrho')$ stems:

$$\begin{aligned}\tilde{\mathcal{R}}(E,\varrho,\varrho')&=\sum_{k,l=1}^{\text{rank N}}\tilde{\Psi}_k(E,\varrho)[\tilde{\underline{\mathsf{S}}}^{-1}(E)]_{kl}\tilde{\Psi}_l^{\dagger}(E,\varrho')\\&=\sum_{i,j=1}^{n}\Theta_i(\varrho)\left[\sum_{k,l=1}^{\text{rank N}}\tilde{a}_{ik}(E)[\tilde{\underline{\mathsf{S}}}^{-1}(E)]_{kl}\tilde{a}_{jl}^*(E)\right]\\&\quad\times\Theta_j^{\dagger}(\varrho'),\end{aligned} \tag{6.89}$$

Here $\tilde{\underline{\mathsf{S}}}(E)$ is a Hermitian matrix of dimensions rank N$\times$rank N, elements of which are given by

$$\tilde{\underline{S}}_{kl}(E)=(\tilde{\Psi}_k|\nabla_n\tilde{\Psi}_l)_{\mathfrak{S}}+\frac{2m}{\hbar^2}\langle\tilde{\Psi}_k|[\hat{\mathcal{H}}-E]\tilde{\Psi}_l\rangle_{\mathfrak{V}} \tag{6.90}$$

or, equivalently, after substituting Eq. (6.79), by

$$\tilde{\underline{S}}_{kl}(E)=\tilde{\mathbf{a}}_k^{\dagger}(E)\mathsf{S}(E)\tilde{\mathbf{a}}_l(E), \tag{6.91}$$

where $\mathsf{S}(E)$ is the Hermitian $n\times n$ matrix defined by Eq. (6.4). [The matrices $\tilde{\mathsf{S}}(E)$ and $\tilde{\underline{\mathsf{S}}}(E)$ defined by Eqs. (6.57) and (6.90), respectively, in general will be different; cf. the remark following Eq. (6.83).]

Since, in general, the matrix $\tilde{\underline{\mathsf{S}}}(E)$ is not a diagonal one, the relations (6.88) and (6.89) will not be suitable for use for practical purposes. Instead, it will be more convenient to approximate $\hat{\mathcal{R}}(E)$ by the operator $\hat{\tilde{\underline{\mathfrak{R}}}}(E)$ with the kernel [cf. Eq. (3.35)]

$$\begin{aligned}\tilde{\underline{\mathfrak{R}}}(E,\varrho,\varrho')&=\sum_{k=1}^{\text{rank N}}\nabla_n\tilde{\Psi}_k(E,\varrho)[\widetilde{b_k^{-1}}(E)]^3\nabla_n\tilde{\Psi}_k^{\dagger}(E,\varrho')\\&=\sum_{i,j=1}^{n}\nabla_n\Theta_i(\varrho)\\&\quad\times\left[\sum_{k=1}^{\text{rank N}}\tilde{a}_{ik}(E)[\widetilde{b_k^{-1}}(E)]^3\tilde{a}_{jk}^*(E)\right]\nabla_n\Theta_j^{\dagger}(\varrho').\end{aligned} \tag{6.92}$$

From Eqs. (6.87), (6.92), and (6.80) one deduces that $\hat{\tilde{\underline{\mathfrak{R}}}}(E)$ is the inverse of $\hat{\tilde{\underline{\mathcal{B}}}}(E)$ in the sense that

$$\hat{\tilde{\underline{\mathcal{B}}}}(E)\hat{\tilde{\underline{\mathfrak{R}}}}(E)=\hat{\tilde{\underline{\mathfrak{R}}}}(E)\hat{\tilde{\underline{\mathcal{B}}}}(E)=\hat{\tilde{\mathcal{A}}}_{\mathfrak{S}}(E), \tag{6.93}$$

where the operator $\hat{\tilde{\mathcal{A}}}_{\mathfrak{S}}(E)$, with the kernel [cf. Eq. (3.27)]

$$\tilde{\mathcal{A}}_{\mathfrak{S}}(E,\varrho,\varrho')=\sum_{k=1}^{\text{rank N}}\nabla_n\tilde{\Psi}_k(E,\varrho)[\widetilde{b_k^{-1}}(E)]^2\nabla_n\tilde{\Psi}_k^{\dagger}(E,\varrho'), \tag{6.94}$$

is the projector on the subspace of $\mathcal{A}_{\mathfrak{S}}(E)$ spanned by the approximate eigenfunctions $\{\tilde{\Psi}_k(E,\varrho)\}$, $(k=1,2,\ldots,\text{rank N})$. We emphasize, however, that estimate (6.92) has the deficiency of *not* being a variational one.

VII. USE OF THE SLATER DETERMINANTAL BASIS FUNCTIONS

Although the basis functions $\{\Theta_i(\mathbf{r})\}$ used in expansions (6.1) and (6.43) may be chosen in a great variety of ways, in applications of the variational *R*-matrix methods to systems with more than two electrons it is most convenient to choose these functions as Slater determinants built of one-electron spin orbitals. Use of such functions facilitates significantly the evaluation of elements of the matrices $\mathsf{S}(E)$, $\mathsf{T}(E)$, M, and N which appeared in Sec. VI.

Let $\{\psi_\alpha(\mathbf{r})\}$, $(\alpha=1,2,\ldots,\mu$ with $\mu\geqslant N)$, be a *given* set

of linearly independent one-electron spin orbitals. Without loss of generality, we assume that they are orthonormal *within the volume* $\mathcal{V}$

$$\langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha\beta}. \tag{7.1}$$

From Kronecker's products of these spin orbitals, with the use of the antisymmetrizer $\hat{\mathcal{A}}_{\mathfrak{V}}$, we may construct $\mu_N = \binom{\mu}{N}$ linearly independent N-electron Slater determinants of the form

$$\begin{aligned}\Theta_i(\mathfrak{r}) &\equiv \Theta_{\{\iota_1\iota_2\ldots\iota_N\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) \\ &= \sqrt{N!}\,\hat{\mathcal{A}}_{\mathfrak{V}}\{\psi_{\iota_1}(\mathbf{r}_1)\otimes\psi_{\iota_2}(\mathbf{r}_2)\otimes\cdots\otimes\psi_{\iota_N}(\mathbf{r}_N)\} \\ &= \frac{1}{\sqrt{N!}}\det|\psi_{\iota_1}(\mathbf{r}_1),\psi_{\iota_2}(\mathbf{r}_2),\ldots,\psi_{\iota_N}(\mathbf{r}_N)|,\end{aligned} \tag{7.2}$$

where we assume $\iota_1 < \iota_2 < \cdots < \iota_N$ to avoid redundancy. Due to the orthonormality property (7.1) of the spin orbitals, the determinants $\{\Theta_i(\mathfrak{r})\}$ form an orthonormal set *within the hypervolume* $\mathfrak{V}$,

$$\langle \Theta_i | \Theta_k \rangle_{\mathfrak{V}} = \delta_{ik}, \tag{7.3}$$

with $i = \{\iota_1\iota_2\ldots\iota_N\}$, $k = \{\kappa_1\kappa_2\ldots\kappa_N\}$ and

$$\delta_{ik} = \delta_{\iota_1\kappa_1}\delta_{\iota_2\kappa_2}\cdots\delta_{\iota_N\kappa_N}. \tag{7.4}$$

From the set $\{\Theta_i(\mathfrak{r})\}$ we choose n, $(1 \leqslant n \leqslant \mu_N)$, determinants (for convenience, they will be assumed to be those with $1 \leqslant i \leqslant n$) which are used as basis functions in estimation procedures described in Secs. VI C and VI D.

The main advantage of the use of the orthonormal Slater determinants (7.2) lies in the ease with which matrix elements of relevant operators between such functions are computed. We define an annihilation operator $\hat{A}_\alpha$ (the index refers to the αth spin orbital, $1 \leqslant \alpha \leqslant \mu$) such that [22]

$$\hat{A}_\alpha \Theta^{(N)}_{\{\iota_1\iota_2\ldots\iota_N\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \begin{cases} (-)^{N+j}\Theta^{(N-1)}_{\{\iota_1\iota_2\ldots\iota_{j-1}\iota_{j+1}\ldots\iota_N\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N-1}) & \text{for } \alpha = \iota_j \in \{\iota_1,\iota_2,\ldots,\iota_N\} \\ 0 \quad \text{for } \alpha \notin \{\iota_1,\iota_2,\ldots,\iota_N\} \end{cases} \tag{7.5}$$

(for the sake of clarity, in the above definition we have added the superscripts in parentheses at the Θ's referring to numbers of electrons described by these functions). The annihilators defined in that way anticommute:

$$\hat{A}_\alpha\hat{A}_\beta + \hat{A}_\beta\hat{A}_\alpha = 0. \tag{7.6}$$

It follows from the well-known properties of determinants that

$$\begin{aligned}\Theta_i(\mathfrak{r}) &= \frac{1}{\sqrt{N}}\sum_{\alpha=1}^{\mu}[\hat{A}_\alpha\Theta_i(\mathfrak{r})]\otimes\psi_\alpha(\mathbf{r}_N) \\ &= \frac{1}{\sqrt{N(N-1)}}\sum_{\alpha,\beta=1}^{\mu}[\hat{A}_\beta\hat{A}_\alpha\Theta_i(\mathfrak{r})]\otimes\psi_\beta(\mathbf{r}_{N-1}) \\ &\quad\otimes\psi_\alpha(\mathbf{r}_N).\end{aligned} \tag{7.7}$$

Making use of Eqs. (7.1), (7.5), and (7.7), one readily obtains the following expressions for elements of the matrices M, N, $\mathsf{S}(E)$, and $\mathsf{T}(E)$:

$$M_{ij} \equiv (\Theta_i|\Theta_j)_{\mathfrak{S}} = \sum_{\alpha,\beta=1}^{\mu}\gamma^{(ij)}_{\alpha\beta}(\psi_\alpha|\psi_\beta), \tag{7.8}$$

$$N_{ij} \equiv (\nabla_n\Theta_i|\nabla_n\Theta_j)_{\mathfrak{S}} = \sum_{\alpha,\beta=1}^{\mu}\gamma^{(ij)}_{\alpha\beta}(\partial_n\psi_\alpha|\partial_n\psi_\beta), \tag{7.9}$$

$$\begin{aligned}S_{ij}(E) &\equiv (\Theta_i|\nabla_n\Theta_j)_{\mathfrak{S}} + \frac{2m}{\hbar^2}\langle\Theta_i|[\hat{\mathcal{H}}-E]\Theta_j\rangle_{\mathfrak{V}} \\ &= \sum_{\alpha,\beta=1}^{\mu}\gamma^{(ij)}_{\alpha\beta}(\psi_\alpha|\partial_n\psi_\beta) + \frac{2m}{\hbar^2}\sum_{\alpha,\beta=1}^{\mu}\left[\gamma^{(ij)}_{\alpha\beta}\langle\psi_\alpha|\hat{H}\psi_\beta\rangle\right. \\ &\quad\left. + \frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Gamma^{(ij)}_{\alpha\xi,\beta\zeta}\langle\psi_\alpha\psi_\xi|\hat{U}\psi_\beta\psi_\zeta\rangle_{\mathcal{V}^2}\right] - \frac{2mE}{\hbar^2}\delta_{ij}\end{aligned} \tag{7.10}$$

and

$$\begin{aligned}T_{ij}(E) &\equiv (\nabla_n\Theta_i|\Theta_j)_{\mathfrak{S}} - \frac{2m}{\hbar^2}\langle\Theta_i|[\hat{\mathcal{H}}-E]\Theta_j\rangle_{\mathfrak{V}} \\ &= \sum_{\alpha,\beta=1}^{\mu}\gamma^{(ij)}_{\alpha\beta}(\partial_n\psi_\alpha|\psi_\beta) - \frac{2m}{\hbar^2}\sum_{\alpha,\beta=1}^{\mu}\left[\gamma^{(ij)}_{\alpha\beta}\langle\psi_\alpha|\hat{H}\psi_\beta\rangle\right. \\ &\quad\left. + \frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Gamma^{(ij)}_{\alpha\xi,\beta\zeta}\langle\psi_\alpha\psi_\xi|\hat{U}\psi_\beta\psi_\zeta\rangle_{\mathcal{V}^2}\right] + \frac{2mE}{\hbar^2}\delta_{ij},\end{aligned} \tag{7.11}$$

with the numerical coefficients $\gamma^{(ij)}_{\alpha\beta}$ and $\Gamma^{(ij)}_{\alpha\xi,\beta\zeta}$, assuming only values 0 and ± 1, defined as

$$\gamma^{(ij)}_{\alpha\beta} = \langle\hat{A}_\alpha\Theta_i|\hat{A}_\beta\Theta_j\rangle_{\mathcal{V}^{N-1}}, \tag{7.12}$$

$$\Gamma^{(ij)}_{\alpha\xi,\beta\zeta} = \langle\hat{A}_\alpha\hat{A}_\xi\Theta_i|\hat{A}_\beta\hat{A}_\zeta\Theta_j\rangle_{\mathcal{V}^{N-2}}. \tag{7.13}$$

Knowledge of the matrix elements (7.8)–(7.11) suffices to find estimates of eigenvalues and eigenvectors, and consequently also estimates of the kernels of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ [cf. Secs. VI C and VI D].

VIII. MULTICONFIGURATION HARTREE-FOCK APPROACH TO THE *R*-MATRIX METHOD

In Sec. VII it has been presumed that the one-electron spin orbitals $\{\psi_\alpha(\mathbf{r})\}$, of which the determinantal basis functions $\{\Theta_i(\mathfrak{r})\}$ are built, are known in advance. If the spin orbitals are chosen at random from some complete set, a number of Slater determinants $\{\Theta_i(\mathfrak{r})\}$ necessary to obtain convergent results for eigenvalues of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ may be formidable. Hinze and Hamacher [15,2] pointed out, however, that an amount of labor in calculations of eigenvalues of $\hat{\mathcal{B}}(E)$ [and $\hat{\mathcal{R}}(E)$] might be reduced significantly if variational procedures were used not only for determining the best expansion coefficients $\{\overline{a_i}\}$ in Eq. (6.43) but also the optimal forms of the one-electron spin orbitals in a manner similar to that used in multi-configuration Hartree-Fock (MCHF) calculations of atomic and molecular structures. In this section we develop the ideas of Hinze and Hamacher utilizing the unified theory exposed in the preceding sections.

At first let us discuss the case when eigenvalues of $\hat{\mathcal{B}}(E)$ are to be determined. As in Sec. VII, we choose a set of one-electron spin orbitals $\{\overline{\psi}_\alpha(\mathbf{r})\}$, $(\alpha=1,2,\ldots,\mu$, with $\mu \geqslant N)$ but do *not* prescribe their forms apart from imposing the orthonormality constraints

$$\langle \overline{\psi}_\alpha | \overline{\psi}_\beta \rangle = \delta_{\alpha\beta}. \tag{8.1}$$

These spin orbitals are used to construct $\mu_N=\binom{\mu}{N}$ orthonormal N-electron Slater determinants

$$\overline{\Theta}_i(\mathfrak{r}) = \frac{1}{\sqrt{N!}} \det|\overline{\psi}_{\iota_1}(\mathbf{r}_1), \overline{\psi}_{\iota_2}(\mathbf{r}_2), \ldots, \overline{\psi}_{\iota_N}(\mathbf{r}_N)|. \tag{8.2}$$

From the latter set we choose n $(1 \leqslant n \leqslant \mu_N)$ determinants which constitute a basis for the expansion

$$\overline{\Psi}(\mathfrak{r}) = \sum_{i=1}^{n} \overline{a_i} \overline{\Theta}_i(\mathfrak{r}), \tag{8.3}$$

which on the hypersurface $\mathfrak{S}$ approximates some eigenfunction of $\hat{\mathcal{B}}(E)$. The bars over the spin orbitals, inducing the bars over the Slater determinants, feature the fact that optimal forms of the spin orbitals, together with the best values of the expansion coefficients $\{\overline{a_i}\}$, are to be found.

Before we use the variational principle (5.1), we have to modify the functional involved in order to take into account the orthonormality constraints (8.1). As usual, this is done with the aid of undetermined Lagrange multipliers $\{\overline{\lambda}_{\alpha\beta}\}$ (optimal values of which are to be found) and this results in the functional

$$F[\overline{\Psi}, \{\overline{\lambda}_{\alpha\beta}\}] = \frac{(\overline{\Psi}|\nabla_n \overline{\Psi})_{\mathfrak{S}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}} + \frac{2m}{\hbar^2} \frac{\langle \overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}} + \frac{\sum_{\alpha,\beta=1}^{\mu} \overline{\lambda}_{\alpha\beta}[\langle \overline{\psi}_\alpha | \overline{\psi}_\beta \rangle - \delta_{\alpha\beta}]}{(\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}. \tag{8.4}$$

On evaluating the relevant matrix elements as in Sec. VII, this functional may be rewritten in the form

$$F[\{\overline{a_i}\}, \{\overline{\psi}_\alpha\}, \{\overline{\varepsilon}_{\alpha\beta}\}] = \frac{\sum_{i,j=1}^{n} \overline{a_i}^* \overline{a_j} \sum_{\alpha,\beta=1}^{\mu} \gamma_{\alpha\beta}^{(ij)} (\overline{\psi}_\alpha | \partial_n \overline{\psi}_\beta)}{\sum_{i,j=1}^{n} \overline{a_i}^* \overline{a_j} \sum_{\alpha,\beta=1}^{\mu} \gamma_{\alpha\beta}^{(ij)} (\overline{\psi}_\alpha | \overline{\psi}_\beta)}$$
$$+ \frac{2m}{\hbar^2} \frac{\sum_{i,j=1}^{n} \overline{a_i}^* \overline{a_j} \left[\sum_{\alpha,\beta=1}^{\mu} \left(\gamma_{\alpha\beta}^{(ij)} \langle \overline{\psi}_\alpha | \hat{H} \overline{\psi}_\beta \rangle + \frac{1}{2} \sum_{\xi,\zeta=1}^{\mu} \Gamma_{\alpha\xi,\beta\zeta}^{(ij)} \langle \overline{\psi}_\alpha \overline{\psi}_\xi | \hat{U} \overline{\psi}_\beta \overline{\psi}_\zeta \rangle_{\mathcal{V}^2} \right) - E\delta_{ij} \right]}{\sum_{i,j=1}^{n} \overline{a_i}^* \overline{a_j} \sum_{\alpha,\beta=1}^{\mu} \gamma_{\alpha\beta}^{(ij)} (\overline{\psi}_\alpha | \overline{\psi}_\beta)}$$
$$- \frac{2m}{\hbar^2} \frac{\sum_{\alpha,\beta=1}^{\mu} \overline{\varepsilon}_{\alpha\beta} [\langle \overline{\psi}_\alpha | \overline{\psi}_\beta \rangle - \delta_{\alpha\beta}]}{\sum_{i,j=1}^{n} \overline{a_i}^* \overline{a_j} \sum_{\alpha,\beta=1}^{\mu} \gamma_{\alpha\beta}^{(ij)} (\overline{\psi}_\alpha | \overline{\psi}_\beta)}, \tag{8.5}$$

highlighting its explicit dependence on the expansion coefficients and the spin orbitals. For the sake of later convenience, progressing from Eq. (8.4) to Eq. (8.5), we have substituted

$$\overline{\varepsilon}_{\alpha\beta}=-\frac{\hbar^2}{2m}\overline{\lambda}_{\alpha\beta}. \tag{8.6}$$

Subjecting the functional (8.5) to variations in its arguments, from the variational principle

$$\delta F[\{\tilde{a}_i\},\{\tilde{\psi}_\alpha\},\{\tilde{\varepsilon}_{\alpha\beta}\}]=0, \tag{8.7}$$

we derive the following set of multiconfiguration Hartree-Fock equations determining the optimal expansion coefficients $\{\tilde{a}_i\}$, the optimal spin orbitals $\{\tilde{\psi}_\alpha(\mathbf{r})\}$, the optimal Lagrange multipliers $\{\tilde{\varepsilon}_{\alpha\beta}\}$ and the best approximation

$$\tilde{b}=F[\{\tilde{a}_i\},\{\tilde{\psi}_\alpha\},\{\tilde{\varepsilon}_{\alpha\beta}\}] \tag{8.8}$$

to a particular eigenvalue of $\hat{\mathcal{B}}(E)$ we are focusing on

$$\sum_{j=1}^{n}[\tilde{S}_{ij}-\tilde{b}\,\tilde{M}_{ij}]\tilde{a}_j=0, \tag{8.9}$$

$$\sum_{\beta=1}^{\mu}\tilde{\gamma}_{\alpha\beta}\hat{H}(\mathbf{r})\widetilde{\psi_\beta}(\mathbf{r})+\sum_{\beta,\xi,\zeta=1}^{\mu}\tilde{\Gamma}_{\alpha\xi,\beta\zeta}\langle\tilde{\psi}_\xi|\hat{U}\tilde{\psi}_\zeta\rangle\tilde{\psi}_\beta(\mathbf{r})=\sum_{\beta=1}^{\mu}\tilde{\varepsilon}_{\alpha\beta}\tilde{\psi}_\beta(\mathbf{r})\quad(\text{in }\mathcal{V}), \tag{8.10}$$

$$\sum_{\beta=1}^{\mu}\tilde{\gamma}_{\alpha\beta}[\partial_n\tilde{\psi}_\beta(\boldsymbol{\rho})-\tilde{b}\tilde{\psi}_\beta(\boldsymbol{\rho})]=0\quad(\text{on }\mathcal{S}) \tag{8.11}$$

and

$$\langle\tilde{\psi}_\alpha|\tilde{\psi}_\beta\rangle=\delta_{\alpha\beta}, \tag{8.12}$$

with

$$\tilde{M}_{ij}=\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\tilde{\psi}_\alpha|\tilde{\psi}_\beta) \tag{8.13}$$

and

$$\tilde{S}_{ij}=\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\tilde{\psi}_\alpha|\partial_n\tilde{\psi}_\beta)+\frac{2m}{\hbar^2}\sum_{\alpha,\beta=1}^{\mu}\left[\gamma_{\alpha\beta}^{(ij)}\langle\tilde{\psi}_\alpha|\hat{H}\tilde{\psi}_\beta\rangle+\frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Gamma_{\alpha\xi,\beta\zeta}^{(ij)}\langle\tilde{\psi}_\alpha\tilde{\psi}_\xi|\hat{U}\tilde{\psi}_\beta\tilde{\psi}_\zeta\rangle_{\mathcal{V}^2}\right]-\frac{2mE}{\hbar^2}\delta_{ij} \tag{8.14}$$

[the $n\times n$ matrix $\tilde{\mathsf{S}}$ composed of the elements (8.14) should not be confused with the matrix defined by Eq. (6.57)], where

$$\tilde{\gamma}_{\alpha\beta}=\sum_{i,j=1}^{n}\tilde{a}_i^*\gamma_{\alpha\beta}^{(ij)}\tilde{a}_j \tag{8.15}$$

and

$$\tilde{\Gamma}_{\alpha\xi,\beta\zeta}=\sum_{i,j=1}^{n}\tilde{a}_i^*\Gamma_{\alpha\xi,\beta\zeta}^{(ij)}\tilde{a}_j, \tag{8.16}$$

with $\gamma_{\alpha\beta}^{(ij)}$ and $\Gamma_{\alpha\xi,\beta\zeta}^{(ij)}$ defined by Eqs. (7.12) and (7.13), respectively. We stress that although the notation used in this section does not emphasize this fact explicitly, it should be remembered that all quantities marked with the tilde are functions of the energy E.

Although general similarities in the form between the MCHF system (8.9)–(8.12) and the common MCHF systems encountered in computations of atomic and molecular structures [22,23] are evident, there are also significant differences between these systems. First, in the standard MCHF theory one aims to find energy levels, while in the present case the energy E is prescribed. Second, in the standard theory the domain on which spin orbitals are defined is $\mathbb{R}^3$; in the present case the problem is considered in the finite volume $\mathcal{V}\subset\mathbb{R}^3$. Third, in atomic and molecular structure computations spin orbitals are forced to vanish on a boundary of the domain (i.e., at infinity); in the present case on the surface $\mathcal{S}$ enclosing $\mathcal{V}$ spin orbitals obey the boundary conditions (8.11) which are not prescribed (since $\tilde{b}$ is not known in advance but is to be determined in the course of solving the MCHF system, as well). Finally, matrices in algebraic parts of the standard and the present systems are defined differently, and a peculiar feature of the present problem is an unavoidable singularity of the weight matrix $\tilde{\mathsf{M}}$ [cf. the remark following Eq. (6.50)].

Because of their complexity, the finite-volume MCHF equations (8.9)–(8.12) must be solved in an iterative way. The algorithm suggested below is an adaptation of the one used for solving the standard MCHF equations in atomic and molecular structure computations [24].

(i) Obtain starting orthonormal spin-orbitals.

(ii) [Begin the configuration-interaction (CI) cycle] construct and solve the CI equations (8.9).

(iii) Identify the particular eigenvalue $\tilde{b}$ in which you are interested.

(iv*) If the eigenvalue and the corresponding eigenvector are unchanged then *end the CI cycle*; otherwise continue.

(v) Compute the coefficients $\{\tilde{\gamma}_{\alpha\beta}\}$ and $\{\tilde{\Gamma}_{\alpha\xi,\beta\zeta}\}$.

(vi) [Begin the HF cycle] construct the HF equations (8.10).

(vii) Construct the boundary conditions (8.11).

(viii) Solve the resulting boundary-value problem.

(ix) Correct the eigenvalue $\tilde{b}$ using Eq. (8.8).

(x*) If the eigenvalue and the spin-orbitals are unchanged then *end the HF cycle*; otherwise go to step (vi) [end the HF cycle].

(xi) Go to step (ii) [end the CI cycle].

Steps (iv*) and (x*) are to be omitted during the first iterations in the CI and HF cycles, respectively.

The above considerations have been based on the variational principle for eigenvalues of the operator $\hat{\mathcal{B}}(E)$. However we might as well attempt to develop an analogous procedure aimed at determining the best approximations to eigenvalues of $\hat{\mathcal{R}}(E)$. The starting point for such a procedure is the functional

$$F[\overline{\Psi}]=\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})_{\mathfrak{S}}}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}}+\frac{\sum_{\alpha,\beta=1}^{\mu}\overline{\lambda}_{\alpha\beta}[\langle\overline{\psi}_\alpha|\overline{\psi}_\beta\rangle-\delta_{\alpha\beta}]}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})_{\mathfrak{S}}} \tag{8.17}$$

obtained from the functional involved in the variational principle (5.2) after including the orthonormality constraint (8.1). As before, $\{\overline{\lambda}_{\alpha\beta}\}$ are the Lagrange coefficients which are to be determined. Defining, for convenience,

$$\overline{\varepsilon}_{\alpha\beta}=\frac{\hbar^2}{2m}\overline{\lambda}_{\alpha\beta} \tag{8.18}$$

[the difference in signs between the right sides of Eqs. (8.6) and (8.18) is intentional] and substituting the trial function (8.3) into the functional (8.17) yields

$$F[\{\overline{a}_i\},\{\overline{\psi}_\alpha\},\{\overline{\varepsilon}_{\alpha\beta}\}]=\frac{\sum_{i,j=1}^{n}\overline{a}_i^*\overline{a}_j\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\overline{\psi}_\alpha|\overline{\psi}_\beta)}{\sum_{i,j=1}^{n}\overline{a}_i^*\overline{a}_j\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\overline{\psi}_a|\partial_n\overline{\psi}_\beta)}-\frac{2m}{\hbar^2}\frac{\sum_{i,j=1}^{n}\overline{a}_i^*\overline{a}_j\left[\sum_{\alpha,\beta=1}^{\mu}\left(\gamma_{\alpha\beta}^{(ij)}\langle\overline{\psi}_\alpha|\hat{H}\overline{\psi}_\beta\rangle+\frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Gamma_{\alpha\xi,\beta\zeta}^{(ij)}\langle\overline{\psi}_\alpha\overline{\psi}_\xi|\hat{U}\overline{\psi}_\beta\overline{\psi}_\zeta\rangle_{\mathcal{V}^2}\right)-E\delta_{ij}\right]}{\sum_{i,j=1}^{n}\overline{a}_i^*\overline{a}_j\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\overline{\psi}_\alpha|\partial_n\overline{\psi}_\beta)}+\frac{2m}{\hbar^2}\frac{\sum_{\alpha,\beta=1}^{\mu}\overline{\varepsilon}_{\alpha\beta}[\langle\overline{\psi}_\alpha|\overline{\psi}_\beta\rangle-\delta_{\alpha\beta}]}{\sum_{i,j=1}^{n}\overline{a}_i^*\overline{a}_j\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\overline{\psi}_\alpha|\partial_n\overline{\psi}_\beta)}. \tag{8.19}$$

From the variational principle

$$\delta F[\{\tilde{a}_i\},\{\tilde{\psi}_\alpha\},\{\tilde{\varepsilon}_{\alpha\beta}\}]=0, \tag{8.20}$$

one derives the set of MCHF equations

$$\sum_{j=1}^{n}[\tilde{T}_{ij}-\widetilde{b^{-1}}\tilde{N}_{ij}]\tilde{a}_j=0, \tag{8.21}$$

$$\sum_{\beta=1}^{\mu}\tilde{\gamma}_{\alpha\beta}\hat{H}(\mathbf{r})\tilde{\psi}_\beta(\mathbf{r})+\sum_{\beta,\xi,\zeta=1}^{\mu}\tilde{\Gamma}_{\alpha\xi,\beta\zeta}\langle\tilde{\psi}_\xi|\hat{U}\tilde{\psi}_\zeta\rangle\tilde{\psi}_\beta(\mathbf{r})=\sum_{\beta=1}^{\mu}\tilde{\varepsilon}_{\alpha\beta}\tilde{\psi}_\beta(\mathbf{r})\quad(\text{in }\mathcal{V}), \tag{8.22}$$

$$\sum_{\beta=1}^{\mu}\tilde{\gamma}_{\alpha\beta}[\widetilde{b^{-1}}\partial_n\tilde{\psi}_\beta(\boldsymbol{\rho})-\tilde{\psi}_\beta(\boldsymbol{\rho})]=0\quad(\text{on }\mathcal{S}) \tag{8.23}$$

and

$$\langle\tilde{\psi}_\alpha|\tilde{\psi}_\beta\rangle=\delta_{\alpha\beta}, \tag{8.24}$$

with

$$\tilde{N}_{ij}=\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\tilde{\psi}_\alpha|\partial_n\tilde{\psi}_\beta), \tag{8.25}$$

$$\tilde{T}_{ij}=\sum_{\alpha,\beta=1}^{\mu}\gamma_{\alpha\beta}^{(ij)}(\partial_n\tilde{\psi}_\alpha|\tilde{\psi}_\beta)-\frac{2m}{\hbar^2}\sum_{\alpha,\beta=1}^{\mu}\left[\gamma_{\alpha\beta}^{(ij)}\langle\tilde{\psi}_\alpha|\hat{H}\tilde{\psi}_\beta\rangle+\frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Gamma_{\alpha\xi,\beta\zeta}^{(ij)}\langle\tilde{\psi}_\alpha\tilde{\psi}_\xi|\hat{U}\tilde{\psi}_\beta\tilde{\psi}_\zeta\rangle_{\mathcal{V}^2}\right]+\frac{2mE}{\hbar^2}\delta_{ij} \tag{8.26}$$

[elements (8.26) should not be confused with elements of the matrix defined by Eq. (6.63)] and the coefficients $\{\tilde{\gamma}_{\alpha\beta}\}$ and $\{\tilde{\Gamma}_{\alpha\xi,\beta\zeta}\}$ defined by Eqs. (8.15) and (8.16), respectively.

Solving these equations provides us with optimal spin orbitals, expansion coefficients, the Lagrange multipliers, and the best estimates

$$\widetilde{b^{-1}} = F[\{\tilde{a}_i\},\{\tilde{\psi}_\alpha\},\{\tilde{\varepsilon}_{\alpha\beta}\}] \tag{8.27}$$

of eigenvalues of the operator $\hat{\mathcal{R}}(E)$. After obvious modifications, algorithm steps (i)–(xi) may be used for solving the MCHF equations (8.21)–(8.24).

It should be noticed that starting with the same initial guess of the spin orbitals $\{\tilde{\psi}_\alpha(\mathbf{r})\}$, the MCHF systems (8.9)–(8.12) and (8.21)–(8.24) in general will yield *different* final results; the results will be identical only when the number of spin orbitals (and the resulting Slater determinants) increases to infinity. At the present stage, without prior numerical experiments, it is impossible to predict which of the two MCHF systems derived should be preferred in actual computations.

IX. CONCLUSIONS

There are two directions in which we plan to continue the present work. First, we are developing a computer code solving the finite-volume MCHF equations (8.9)–(8.12) and (8.21)–(8.24) for atomic systems. An output from that code will be used in computations of low-energy electron-atom collision and half-collision processes. Second, it is obvious that the theory exposed in this work is applicable only to nonrelativistic systems. To be able to treat electron scattering from heavy atomic targets and their photoionization, the processes in which both direct and indirect relativistic effects are known to be important, one shall need a unified formulation of the variational *R*-matrix theory for many-electron relativistic systems, and, in this connection, the multiconfiguration Dirac-Hartree-Fock *R*-matrix method would be of particular use. Work on this project is also in progress.

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